

U.S. DEPARTMENT OF COMMERCE
National Technical Information Service
PB-277 469

High Purity PNA Hydrocarbons and Other Aromatic Compounds Synthesis and Purification

Oklahoma State Univ, Stillwater Dept of Chemistry

Prepared for

Environmental Sciences Research Lab, Research Triangle Park, N C

Jan 78

EPA-600/2-78-006
January 1978

PB 277 469

Environmental Protection Technology Series

HIGH PURITY PNA HYDROCARBONS AND OTHER AROMATIC COMPOUNDS Synthesis and Purification



Environmental Sciences Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Development, U.S. Environmental Protection Agency, have been grouped into nine series. These nine broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The nine series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies
6. Scientific and Technical Assessment Reports (STAR)
7. Interagency Energy-Environment Research and Development
8. "Special" Reports
9. Miscellaneous Reports

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment, and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

TECHNICAL REPORT DATA
(Please read instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-78-006		2.		3. RECIPIENT'S ACCESSION NO. PB277469	
4. TITLE AND SUBTITLE HIGH PURITY PNA HYDROCARBONS AND OTHER AROMATIC COMPOUNDS Synthesis and Purification				5. REPORT DATE January 1978	
7. AUTHOR(S) E. J. Eisenbraun				6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Oklahoma State University Stillwater, Oklahoma 74074				8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711				10. PROGRAM ELEMENT NO. 1AD605 BE-04(FY-77)	
				11. CONTRACT/GRANT NO. 803097	
15. SUPPLEMENTARY NOTES				13. TYPE OF REPORT AND PERIOD COVERED Final 5-74 to 5-77	
16. ABSTRACT The synthesis and/or purification of a group of polynuclear aromatic (PNA) hydrocarbons commonly found as pollutants in the environment are described. The steps used in a given synthesis, the experiments carried out, and a presentation of some instrumental data obtained in establishing the identity and purity of the hydrocarbons are included. Publications derived from this work are cited.				14. SPONSORING AGENCY CODE EPA-600/09	
17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
*Air pollution *Aromatic polycyclic hydrocarbons *Chemical reactions *Purification				13B 07C 07D	
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC		19. SECURITY CLASS (This Report) UNCLASSIFIED		73 YES	
		20. SECURITY CLASS (This page) UNCLASSIFIED		22. PRICE PCF704/MF901	

EPA-600/2-78-006
January 1978

HIGH PURITY PNA HYDROCARBONS
AND OTHER AROMATIC COMPOUNDS
Synthesis and Purification

by

E.J. Eisenbraun
Department of Chemistry
Oklahoma State University
Stillwater, Oklahoma 74074

Grant No. 803097

Project Officer

James E. Meeker
Atmospheric Chemistry and Physics Division
Environmental Sciences Research Laboratory
Research Triangle Park, North Carolina 27711

ENVIRONMENTAL SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

DISCLAIMER

This report has been reviewed by the Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The synthesis and/or purification of a group of polynuclear aromatic (PNA) hydrocarbons commonly found as pollutants in the environment are described. The steps used in a given synthesis, the experiments carried out, and a presentation of some instrumental data obtained in establishing the identity and purity of the hydrocarbons are included. Publications derived from this work are cited.

This report was submitted in fulfillment of Grant Number 803097 by Oklahoma State University under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1, 1974 to April 30, 1977, and work was completed as of May 1, 1977.

CONTENTS

Abstract	iii
Schemes	vii
Figures	viii
Acknowledgments	ix
1. Introduction	1
2. Conclusions	3
3. Recommendations	4
4. Materials and Methods	6
Hydrocarbons Obtained by Direct Purification -- Purification Techniques and Safety Precautions	6
Purification Techniques -- Recrystallization	6
Purification Techniques -- Picric Acid Complexation	7
Purification Techniques -- Soxhlet Extraction	7
Purification Techniques -- Zone Refining, Liquid Chromatography and Sublimation	10
Safety Measures	11
Analytical Methods	13
Synthesis of Polynuclear Aromatic Hydrocarbons Listed in 1974 Proposal	14
a. Anthanthrene (5)	14
b. Benz[a]anthracene (6)	16
c. Benzo[b]fluoranthene (7)	16
d. Benzo[<u>i</u>]fluoranthene (8)	17
e. Benzo[k]fluoranthene (9)	18
f. Benzo[ghi]perylene (10)	19
g. Benzo[a]pyrene (11)	20
h. Coronene (12)	20
i. Indeno[1,2,3- <u>cd</u>]pyrene (13)	21
j. Perylene (14)	22
k. Triphenylene (15)	22
Hydrocarbons Added Subsequent to the 1974 List	23
Benzo[c]phenanthrene (44)	24
Tetrahydropyrene (46) and Hexahydropyrene (47)	24
1,2,3,4-Tetrahydroanthracene (50)	25

5. Experimental Procedures	26
Purification of Solvents	26
Purification of Chrysene (1), Fluoranthene (2), Pyrene (3), and 1,3,5-Triphenylbenzene (4)	27
Synthesis and Purification of Anthanthrene (5)	28
Synthesis and Purification of Benz[a]anthracene (6)	29
Synthesis and Purification of Benzo[b]fluoranthene (7)	29
Synthesis and Purification of <u>cis,anti</u> -4,5,6,6a,6b,7,8,12b- Octahydrobenzo[<u>j</u>]fluoranthene (27) and Benzo[<u>j</u>]fluoranthene (8)	30
Synthesis and Purification of Benzo[<u>k</u>]fluoranthene (9)	32
Synthesis and Purification of Benzo[<u>ghi</u>]perylene (10)	32
Synthesis and Purification of Benzo[<u>a</u>]pyrene (11)	34
Synthesis of Coronene (12), Indeno[1,2,3- <u>cd</u>]pyrene (13), and Perylene (14)	36
Synthesis and Purification of Triphenylene (15) and <u>s</u> -Dodeca- hydrotriphenylene (40)	36
Synthesis and Purification of Benzo[<u>c</u>]phenanthrene (44)	39
Synthesis of Tetrahydropyrene (46), Hexahydropyrene (47), and 1,2,3,4-Tetrahydroanthracene (50)	40
6. Results and Discussions	55
Footnotes and References	57
List of Theses and Publications	60

SCHMES

<u>Number</u>		<u>Page</u>
1	Anthanthrene (5)	15
2	Benz[a]anthracene (6)	16
3	Benzo[b]fluoranthene (7)	17
4	Benzo[j]fluoranthene (8)	18
5	Benzo[k]fluoranthene (9)	19
6	Benzo[ghi]perylene (10)	19
7	Benzo[a]pyrene (11)	20
8	Coronene (12)	21
9	Indeno[1,2,3-cd]pyrene (13)	21
10	Perylene (14)	22
11	Triphenylene (15)	22
12	Benzo[c]phenanthrene (44)	24
13	Tetrahydropyrene (46) and Hexahydropyrene (47)	25
14	1,2,3,4-Tetrahydroanthracene (50)	25

FIGURES

<u>Number</u>		<u>Page</u>
1	Soxhlet apparatus used to purify PNA hydrocarbons through absorption on alumina and as a picric acid column	8
2	Improved Soxhlet apparatus used in the purification of PNA hydrocarbons	9
3	Apparatus for sublimation of PNA compounds	11
4	Apparatus for increased safety in extraction of PNA hydrocarbons	12
5	Apparatus to clean sintered-glass funnels	13
6	PMR Fourier transform spectrum of chrysene (1) in CDCl ₃ at 100 MHz	41
7	Proton magnetic spectrum of fluoranthene (2) at 100 MHz in CDCl ₃	42
8	Proton magnetic spectrum of pyrene (3) at 100 MHz in CDCl ₃	43
9	Proton magnetic spectrum of 1,3,5-triphenylbenzene (4) at 100 MHz in CDCl ₃	44
10	Proton magnetic spectrum of benz[a]anthracene (6) at 100 MHz in CDCl ₃	45
11	Proton magnetic spectrum of benzo[b]fluoranthene (7) at 100 MHz in CDCl ₃	46
12	Proton magnetic spectrum of benzo[j]fluoranthene (8) at 100 MHz in CDCl ₃	47
13	Proton magnetic spectrum of benzo[k]fluoranthene (9) at 100 MHz in acetonitrile	48
14	PMR Fourier transform spectrum of benzo[ghi]perylene (10) in CDCl ₃ at 100 MHz	49
15	Proton magnetic spectrum of benzo[a]pyrene (11) at 100 MHz in CDCl ₃	50
16	Proton magnetic spectrum of triphenylene (15) at 100 MHz in CDCl ₃	51
17	Proton magnetic spectrum of benzo[c]phenanthrene (44) at 100 MHz in CDCl ₃	52
18	Proton magnetic spectrum of <u>cis,anti</u> -4,5,6,6a,6b,7,8,12b-octahydrobenzo[j]fluoranthene (27) at 100 MHz in CDCl ₃	53
19	Proton magnetic spectrum of <u>s</u> -Dodecahydrotriphenylene (40) at 100 MHz in CDCl ₃	54

ACKNOWLEDGMENTS

Drs. N. R. Beller, University of New Mexico, H. H. Chen, University of Texas, and T. Rangarajan, Annamalia University of Madras, India, served as Research Associates.

L. L. Ansell, Ph.D. 1976, F. U. Ahmed, M.S. 1975, and A. R. Taylor, M.S. 1974, received partial support from the project in obtaining their degrees.

C. E. Browne, D. L. Bymaster, K. D. Cowan, A. G. Holba, H. Storr, E. H. Vickery, and P. Vuppalapaty also have received partial support.

As spokesman for the group, the Principal Investigator gratefully acknowledges the financial assistance these chemists received from the Environmental Protection Agency.

During the early phase of the study, the American Petroleum Institute provided some joint assistance and permitted use of equipment and supplies to further the work. We are grateful for this help. In a similar manner, our current synthesis effort for the Thermodynamics Research Group of the U. S. ERDA station at Bartlesville, Oklahoma allows for shared facilities and some joint effort.

Our project received invaluable assistance from the Analytical Division of the Continental Oil Company, Gulf Research and Development Co., Exxon Research and Engineering Co., and Battelle, Pacific Northwest Laboratories in the form of mass spectrometric, nmr, and liquid chromatographic determinations.

Other mass and nmr determinations were obtained from Oklahoma State University Chemistry Department instruments. The use of the Varian XL-100 nmr spectrometer obtained through NSF Grant CHE76-05571 is gratefully acknowledged.

We thank Mr. James E. Meeker and Dr. E. Sawicki of the Chemistry and Physics Laboratory, Environmental Sciences Research Laboratory, Research Triangle Park, North Carolina and the personnel of the Office of Research Operations, Oklahoma State University, for courteous and helpful assistance.

SECTION 1

INTRODUCTION

This research project was initiated in response to a need expressed by the Chemistry and Physics Laboratory, National Environmental Research Center, Research Triangle Park, North Carolina 27711, for 10-gram samples of pure polynuclear aromatic compounds to be used as instrumental standards.

The alphabetized list of the desired aromatic compounds with their current status follows:

acridine ^a	benzo[<u>a</u>]pyrene ^b
anthanthrene ^b	benzo[<u>g</u>]pyrene ^c
benz[<u>a</u>]acridine ^d	chrysene ^a
benz[<u>c</u>]acridine ^d	coronene ^c
benz[<u>a</u>]anthracene ^b	fluoranthene ^a
benzo[<u>b</u>]fluoranthene ^b	dibenzo[<u>a,h</u>]anthracene ^d
benzo[<u>j</u>]fluoranthene ^b	pyrene ^a
benzo[<u>k</u>]fluoranthene ^b	indeno[1,2,3- <u>cd</u>]pyrene ^c
benzo[<u>mno</u>]fluoranthene ^d	perylene ^c
11H-benzo[<u>b</u>]fluorene ^d	1,3,5-triphenylbenzene ^a
benzo[<u>ghi</u>]perylene ^b	triphenylene ^b

^aPurified from commercial material and shipped. ^bSynthesized and shipped. ^cCurrent work. ^dFuture work.

During the past three years we have synthesized and/or purified 12 hydrocarbons from the above list and are continuing work on several other

ones as indicated. Also, we have supplied benzo[c]phenanthrene as an additional hydrocarbon requested by the sponsor. In addition, we have supplied two other related hydrocarbons which became available as part of the project work or resulted from synthesis carried out for the American Petroleum Institute and/or the Energy Research Development Administration. This total of 15 hydrocarbons prepared as project effort, particularly the completely aromatic ones, are of the type found as products of combustion, petroleum refining, and in the exhaust of automobile engines.

Thus the reported work divides itself into purification of four hydrocarbons available from commercial sources, and synthesis and purification of eleven other hydrocarbons.

SECTION 2

CONCLUSIONS

It is well accepted that PNA hydrocarbons and related aromatic compounds are ubiquitous in their environmental distribution. Despite efforts to control and reduce their presence, there is a good possibility that this distribution in the environment will actually increase until more effective control is realized. We base this assumed increase on several factors -- increased use of aromatic hydrocarbons in an increasing number of internal combustion engines, projected increase in burning of coal, increased use of heavy oils for space heating, projected processing of coal to coal liquids and subsequent increased use of coal oils, and finally, frequent report of oil spills and other disasters which release hydrocarbons to the environment.

This gloomy view is offset by the results of increased efforts to control handling and usage and by improvements in technology. Consequently, since reference PNA compounds occupy a central position in studying and gaining an understanding of environmental problems raised by their presence, it follows that there will be an increased need for such materials. Since many of these hydrocarbons are not available in adequate purity and quantity, it becomes desirable to affect their synthesis to alleviate this need.

SECTION 3

RECOMMENDATIONS

In the preceding section it was pointed out that the need for pure PNA hydrocarbons will probably increase. This projected need may, in part, be met by commercial suppliers. However, PNA hydrocarbons from some commercial sources may contain difficultly removed impurities, as is usually the case for compounds derived from coal tar and coking operations. Thus, it becomes preferable in many cases to synthesize hydrocarbons rather than use commercially available ones in obtaining pure samples.

Future work in this area should be preceded by a list of needed compounds, as was done in this project. This list should contain more compounds than are to be synthesized so that alternate synthesis possibilities can be developed to replace syntheses or purifications which fail or become too expensive for practical completion.

The information as to which structures should be selected for synthesis is dependent on which compounds are considered to be important in the field and whether they are commercially available. Those PNA hydrocarbons which are products of combustion and prominent members of petroleum residues appear to be most important. However, as the utilization of coal increases and coal liquids become more important, other structural types will obviously emerge. Therefore, long-term studies involving polynuclear aromatic compounds found in the environment should include compounds found

to be constituents of coal liquids and the end products of coal liquid utilization.

Since the instrumental capability for detecting and measuring stable (non-radioactive) isotopes of carbon, nitrogen, and oxygen is now rapidly maturing, and such instrumentation is becoming widespread, and further, since stable isotopes are becoming more plentiful and in some cases cheaper, a program should be considered which provides for the systematic synthesis of appropriately labelled compounds.¹ The selection of structures would present a difficult choice. However, some PNA compounds which are most frequently encountered in environmental problems but are not commercially available as labelled materials could be considered for initial synthesis. Compounds containing a greater than normal abundance of stable isotopes have an advantage over those containing unstable isotopes in that their use as tagged molecules in environmental studies does not raise the health problems associated with radioactive tracers. In addition, tagged reference compounds containing stable isotopes can be expected to have good shelf life.

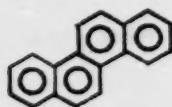
SECTION 4

MATERIALS AND METHODS

The PNA hydrocarbons cited below are divided into three categories of synthesis and purification in order to present a division of the effort involved in the preparation of the pure samples and to connect their relationship to the original proposal.

HYDROCARBONS OBTAINED BY DIRECT PURIFICATION -- PURIFICATION TECHNIQUES AND SAFETY PRECAUTIONS

Hydrocarbons 1 → 4 were commercially available at a reasonable cost and were thus purified without further modification. Their structures and the amount supplied follow:



Chrysene (1)

10.6 g.



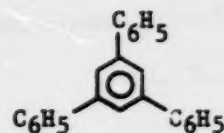
Fluoranthene (2)

10.4 g.



Pyrene (3)

13.5 and 8.3 g.



1,3,5-Triphenyl-
benzene (4)

11.6 g.

Purification Techniques -- Recrystallization

In general, purification of commercial PNA hydrocarbons, many of which are derived from coal tar, is difficult, and more extensive processing is frequently required than for PNA hydrocarbons obtained from synthesis.

The usual route to purification, since PNA hydrocarbons are solids, is to first crystallize from common solvents, e.g., benzene, toluene, isohexane,

methanol, ethanol, and possibly chloroform or dichloromethane. These solvents must either be pure commercial solvents or solvents reprocessed from cheaper grades.

Because of the volumes of solvents required and to reduce the costs, we redistill and reprocess our solvents before use. This usually involves distilling from glass vessels and may include prior treatment with sulfuric acid, silica gel, and/or alumina or other adsorbing agents.

Once it is established through instrumental studies (gc, lc, nmr, mass spectrometry) that recrystallization does not offer additional purification, we usually try complex formation as the next step.

Purification Techniques -- Picric Acid Complexation

Picric acid is usually the best choice for preparation of a complex with a PNA hydrocarbon because of its broad effectiveness and lower cost. 1,3,5-Trinitrobenzene is effective but expensive. 2,4,7-Trinitro-9-fluorenone is also effective, but as with 1,3,5-TNB, is expensive and has the added disadvantage of being a suspected carcinogen.

A common procedure in utilizing picric acid is to mix the aromatic hydrocarbon and picric acid as solutions in 95% ethanol and then allow the resulting picrate complex to crystallize. The crystalline complex is filtered and recrystallized from 95% ethanol or other common solvent. To recover the aromatic hydrocarbon from the complex, the complex may be dissociated by treating with aqueous ammonium or sodium hydroxide and then extracting with ether or by using the Soxhlet extraction technique described in the following section.

Purification Techniques -- Soxhlet Extractions

Prior to our beginning this project, we developed a Soxhlet extraction technique² in which the dried picrate-organic hydrocarbon complex is placed,

as a layer, on top of a column of basic alumina contained in a Soxhlet apparatus similar to that in Fig. 1. The picrate-organic hydrocarbon complex is then extracted with isohexane to leach out the PNA hydrocarbon which, in turn, readily elutes through the basic alumina into the collection flask. Since picric acid is insoluble in isohexane, it remains behind as a layer above the alumina. However, if benzene or more polar solvents are used, picric acid will dissolve and considerably more alumina is required.

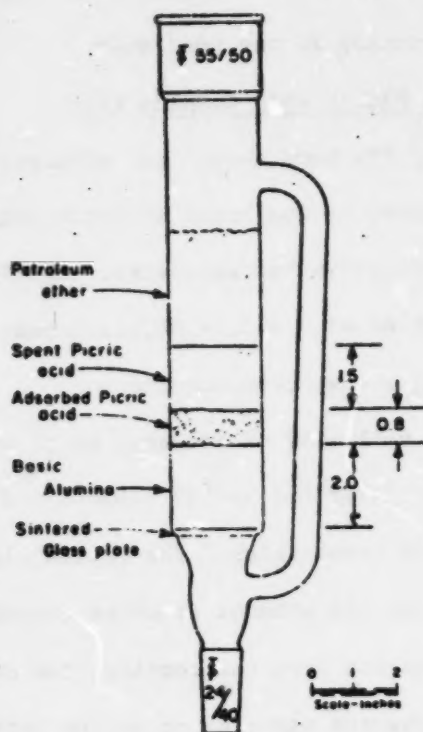


Figure 1. Soxhlet apparatus used to purify PNA hydrocarbons through absorption on alumina and as a picric acid column.

Recently we have improved the Soxhlet apparatus³ (current design is shown in Fig. 2) to include a Teflon stopcock which enables control of liquid level in the Soxhlet apparatus. In many cases it is desirable to keep the picrate covered with a liquid layer to increase efficiency of extraction through direct contact with liquid, but also to increase the flow rate as a result of pressure developed from the liquid head.

This new Soxhlet apparatus has enabled us to develop an efficient and safer approach to the separation and purification of PNA hydrocarbons. In

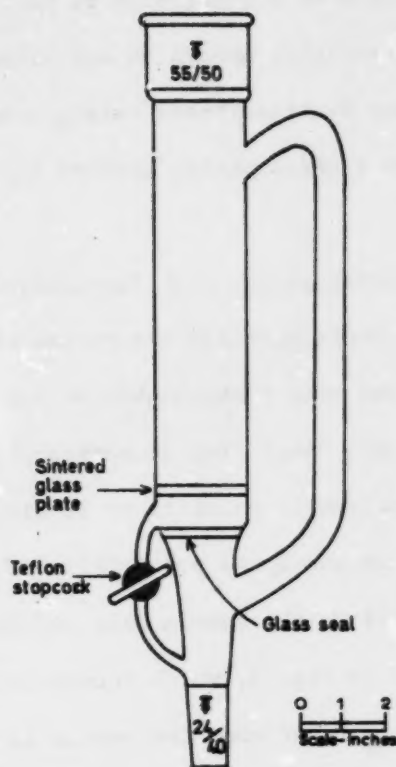


Figure 2. Improved Soxhlet apparatus used in the purification of PNA hydrocarbons

this use, the lower portion of the Soxhlet chamber is charged with basic alumina, which in turn is covered with a layer of lightly tamped picric acid. The hydrocarbon mixture is then layered above the picric acid. Refluxing hexane or benzene dissolves the hydrocarbon mixture and introduces it onto the picric acid. Those hydrocarbons which are capable of picrate formation are retained, whereas those which do not form a picrate or a less firmly complexed picrate migrate rapidly through the picric acid and alumina layers and are eluted first into the collection flask.⁴

Purification Techniques - Zone Refining, Liquid Chromatography and Sublimation

We have used zone refining as a final step in purification. Our experience has shown that a zone-refining apparatus operating with a vertical tube is much more reliable, since vertical tubes rarely break during operation, whereas our attempts to use a horizontally mounted apparatus usually resulted in a ruptured tube.

We have used liquid chromatography (lc) for analysis, but not for purification of samples. Our future purification procedures may include preparative lc, since we now have such instrumentation available.

Sublimation is usually the final step in purification of a PNA hydrocarbon, to insure that no polymeric material or detritus remains. To provide a sublimed sample and to avoid the possibility of rubber particles or stopcock grease being carried to the sample when vacuum is released, we devised the apparatus shown in Fig. 3, which incorporates a sintered glass disc to act as a filtration barrier when the vacuum is released. The O-ring seal removes the need for using stopcock grease with the ball joint.

Examples in which these techniques were used are presented in the Experimental Section.

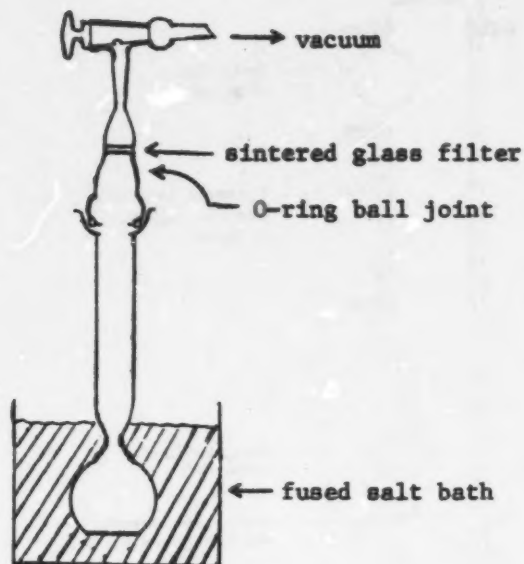


Figure 3. Apparatus for sublimation of PNA compounds

Safety Measures

Since several of the hydrocarbons described in this report are known or suspected carcinogens, we have stressed careful handling of materials to avoid personal contact during synthesis, purification and packaging. We have attempted to develop a safety concept which includes careful planning of experiments and handling. This includes monitoring activities with UV lamps to detect spilled material through fluorescence.

It is our standing policy to have our chemists wear aprons, gloves, surgical face masks and sleeve protection when exposure is eminent. During the packaging of the solid hydrocarbons, we use disposable glove bags and an inert gas (nitrogen or argon) to avoid personal contact.

As an added safety measure we routinely incorporate stainless steel catch basins in the apparatus setup as in Fig. 4 to reduce the chance for contamination of the laboratory should glassware become cracked or broken

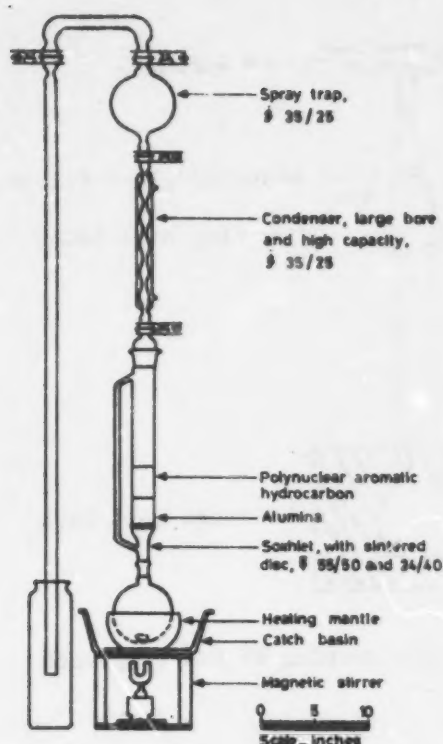


Figure 4. Apparatus for increased safety in extraction of PNA hydrocarbons.

during a reaction. In addition, we also equip apparatus with appropriate collection traps as shown in Fig. 4, so that if bumping or a sudden surge of vapor and/or liquid results during an extraction or reaction, the material flooding through the condenser will harmlessly spill into a collection chamber rather than spray out into the lab.⁵

To minimize contamination of samples during purification, we have found the apparatus shown in Fig. 5 to be useful in cleaning Buchner funnels.⁶ As an added precaution, any glassware including sintered-glass funnels which has been in contact with carcinogenic materials is fired at the annealing temperature to burn off any carbon. This insures that no carcinogenic material survives and that there is no cross contamination of samples.

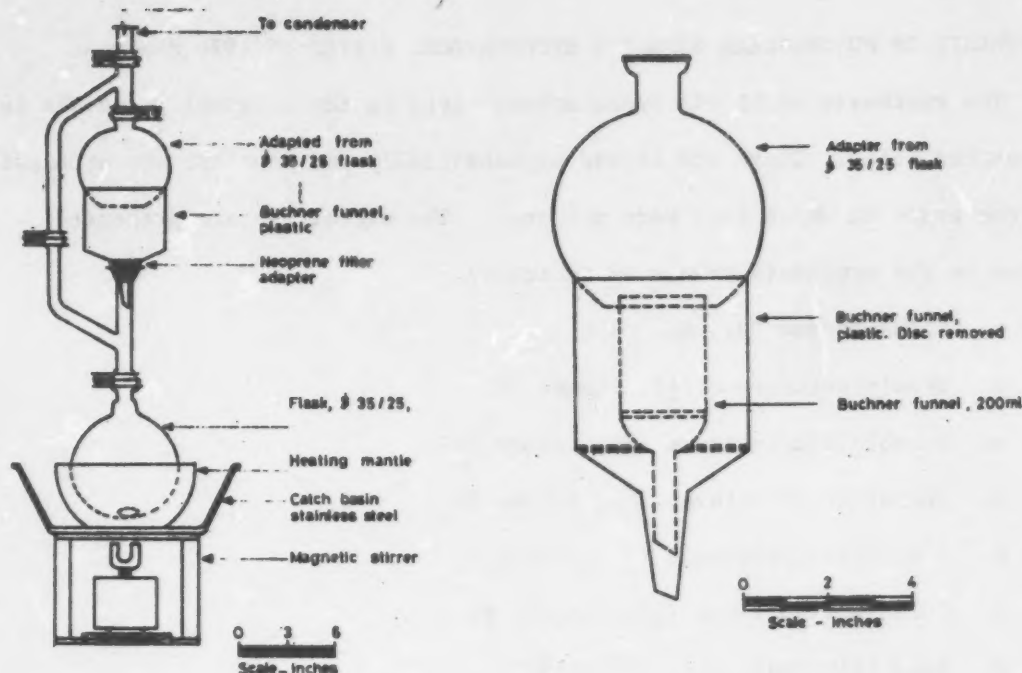


Figure 5. Apparatus to clean sintered-glass funnels.

Analytical Methods

The analysis of the hydrocarbons cited elsewhere in this report and the various intermediates leading to their synthesis was carried out through use of instruments in our laboratories (tlc, glc, and some lc), those of the Chemistry Department (mass spectrometry and nmr) and in some industrial laboratories. The latter are identified under acknowledgments. To avoid repetition, these instruments are cited in Section V, Experimental Procedures.

We have obtained photo-reduced copies of pmr spectra of all hydrocarbons shipped to EPA except anthanthrene (5), which was too insoluble for an adequate spectrum. Chrysene (1) and benzo[ghi]perylene (10) were also too insoluble for conventional pmr spectra. However, use of Fourier-Transform techniques permitted accumulation of pmr spectra for 1 and 10 shown in Fig. 6 and Fig. 14 respectively. Excluding these latter figures, the spectra of the other hydrocarbons are shown in Fig. 7-19.

SYNTHESIS OF POLYNUCLEAR AROMATIC HYDROCARBONS LISTED IN 1974 PROPOSAL

The synthesis of 11 PNA hydrocarbons cited in the original proposals is presented below. These are listed alphabetically and thus are not arranged in the order in which they were prepared. The structures are presented later in the synthesis scheme as indicated.

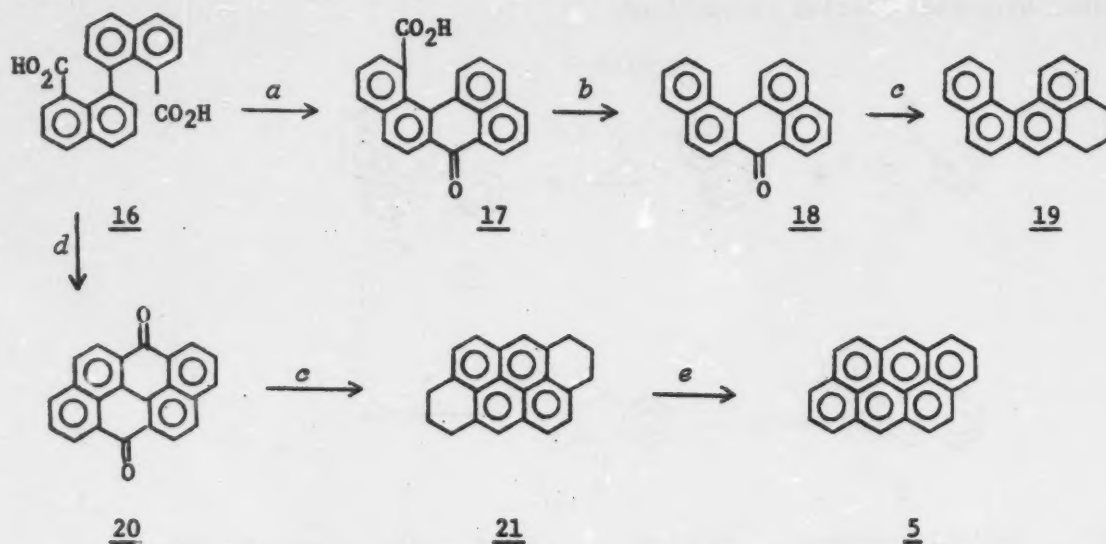
- a. Anthanthrene (5), Scheme I
- b. Benz[a]anthracene (6), Scheme II
- c. Benzo[b]fluoranthene (7), Scheme III
- d. Benzo[j]fluoranthene (8), Scheme IV
- e. Benzo[k]fluoranthene (9), Scheme V
- f. Benzo[ghi]perylene (10), Scheme VI
- g. Benzo[a]pyrene (11), Scheme VII
- h. Coronene (12), Scheme VIII (part of current work)
- i. Indeno[1,2,3-cd]pyrene (13) Scheme IX (part of current work)
- j. Perylene (14), Scheme X (part of current work)
- k. Triphenylene (15), Scheme XI

a. Anthanthrene (5)

Anthanthrene (5) was synthesized as shown in Scheme I. For the most part, this synthesis followed a published procedure.⁷ However, the preparation of 5 presented an opportunity to establish the structure of the new hydrocarbon 21 and to demonstrate that HI-P₄ is a superior reagent in affecting removal of benzylic carbonyl groups,^{8a,b} e.g., 18 → 19 and 20 → 21. Ketone 18 and hydrocarbon 19 were prepared in this work to help establish the structure of the monocyclization product 17. Hydrocarbon 19 was subsequently prepared in an independent synthesis for the American Petroleum Institute.^{8a,b} The new hydrocarbon 21, an intermediate in the synthesis of anthanthrene (5),

was isolated after deoxygenation of diketone 20 with HI-P₄.^{8a,b} The structure of 21 was determined by comparison of its uv spectrum with that of pyrene. These spectra were in good agreement and the expected bathochromic shifts of absorption maxima as the result of the presence of the two saturated rings were observed.

SCHEME 1



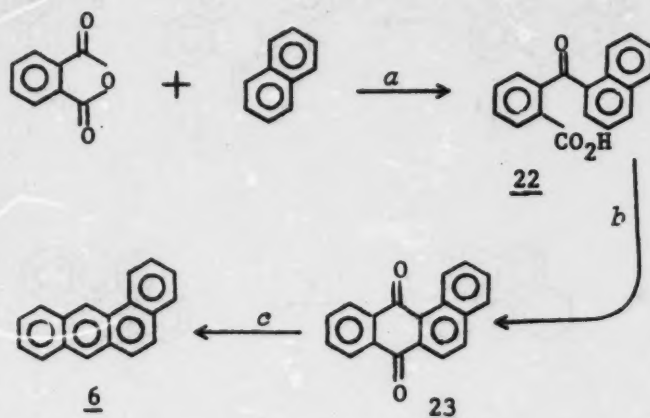
^a ZnCl₂, CH₃CO₂H, Δ. ^b Cu, quinoline, Δ. ^c HI, P₄, CH₃CO₂H, Δ. ^d PPA, Δ.
^e Pd/C, Δ.

A 12.3-g sample of 5 in 33 ampoules and 8 vials was provided.

b. Benz[a]anthracene (6)

This hydrocarbon was prepared using Scheme II. The products of Scheme II were examined in detail and some improvement over published work was realized.⁹ In summary, hot sulfuric acid with added boric acid and liquid HF are inferior to hot PPA in affecting cyclization of 22 to 23.^{10,11,12} We also learned that commercial aluminum isopropoxide was ineffective and that freshly prepared material is required.

SCHEME 2



^a AlCl₃, *o*-dichlorobenzene. ^b PPA, Δ; or H₂SO₄ + H₃BO₃, Δ; or liq. HF.

^c Al[-O-C₆H₁₁]₃, C₆H₁₁OH.

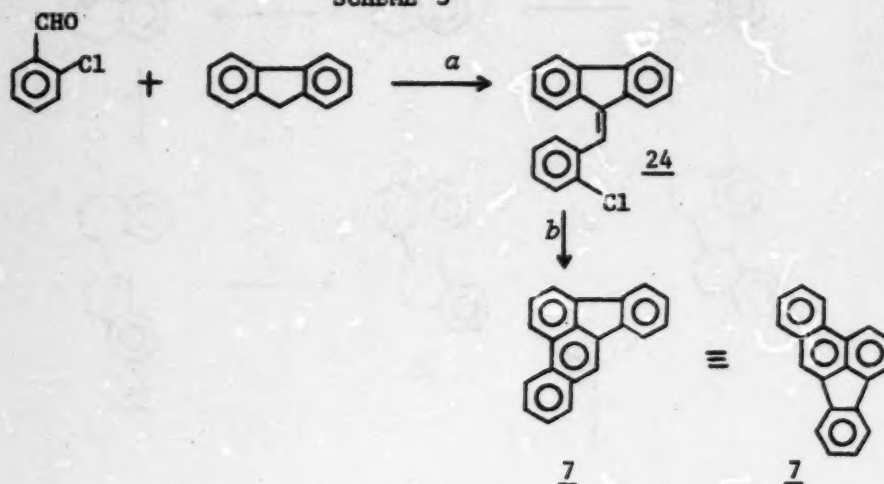
A 13.0-g sample of 6 in 14 vials and 30 ampoules was provided.

c. Benzo[b]fluoranthene (7)

This compound was successfully synthesized as shown in Scheme III.¹³ However, before we used this route, we first made several attempts to carry out the acid-catalyzed cyclization of 9-benzylidene fluorene under a variety of conditions.¹⁴ We had hoped that the preparation of chloro-9-benzylidenefluorene (24) could thus be avoided. We noted that 9-benzylfluorene was a byproduct in the formation of 9-benzylidenefluorene. Presumably the reaction of benzaldehyde and alkali (Cannizzaro conditions) causes this

reaction.¹⁴ We also tried photocyclization of 9-benzylidene fluorene without results.¹⁴

SCHEME 3



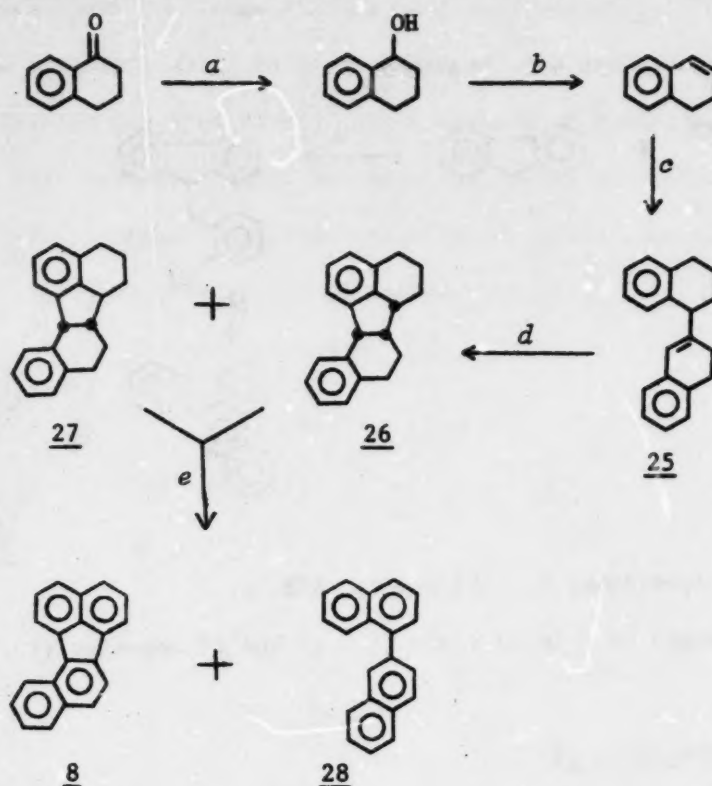
^a Xylene, KOH, piperidine, Δ . ^b Quinoline, KOH, Δ .

A 15.2-g sample of 7 in 13 vials (4.5 g) and 29 ampoules (10.7 g) was provided.

d. Benzo[1]fluoranthene (8)

This hydrocarbon resulted from the extension of an earlier study of the octahydrobenzo[1]fluoranthenes 26 and 27 shown in Scheme IV.¹⁵ Aromatization of pure 26 or 27 or a mixture leads to the yellow-colored 8. If 25 is present, it is converted to 28 which is difficult to remove. The conditions for formation of 25 and/or cyclization to 6 and 27 were studied. Amberlyst-15 does not yield the same mixture of 26 and 27 as is obtained with other acidic reagents (PPA, P_2O_5 , H_2SO_4).^{15,16}

SCHEME 4



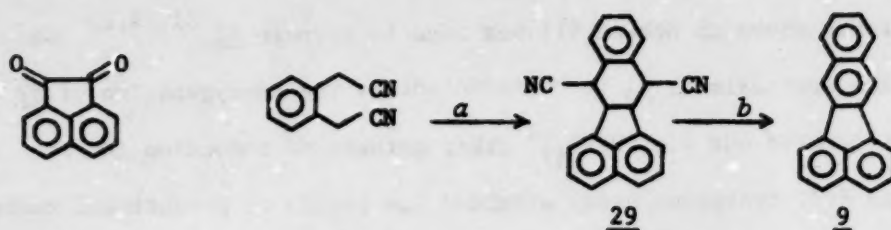
^a(*i*bu)₂AlH. ^bOxalic acid, Δ. ^cAmberlyst-15, C₆H₅. ^dc, Δ. ^ePd/C, Δ.

A 10.1 g sample of 8 in 88 vials was provided.

e. Benzo[k]fluoranthene (9)

Hydrocarbon 9 was prepared by a known procedure involving condensation of acenaphthenequinone and *o*-phenylenediacetonitrile as shown in Scheme V.^{17,18} This led to the dicyanobenzo[k]fluoranthene (33) which was subsequently hydrolyzed and decarboxylated to 10 by heating in the presence of phosphoric acid.

SCHEME 5



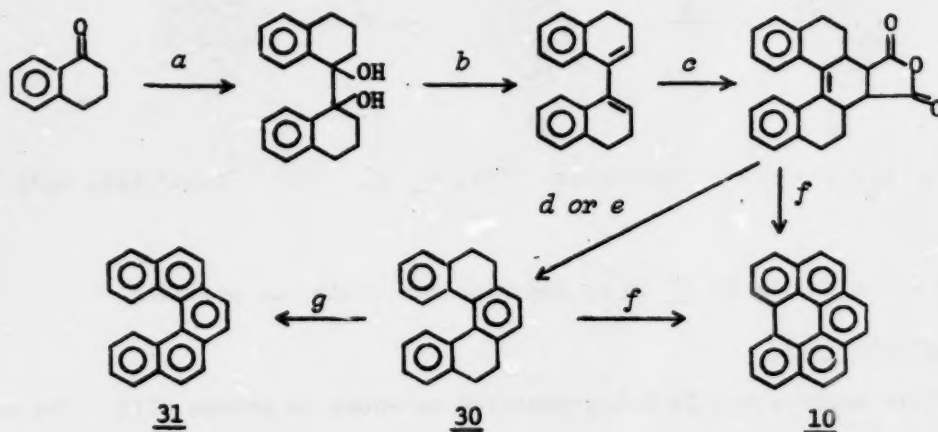
^aAniline, Δ . ^bH₃PO₄, Δ .

A 10.3-g sample of 9 in 47 ampoules (5.6 g) and 19 vials (4.7 g) was provided.

f. Benzo[ghi]perylene (10)

This hydrocarbon was synthesized via Scheme VI from 1-tetralone.^{19,20} As indicated in the scheme, this synthesis route is capable of providing 5,6,9,10-tetrahydridibenzo[cd]phenanthrene (30) and dibenzo[cd]phenanthrene (31) as well as the target hydrocarbon benzo[ghi]perylene (10).

SCHEME 6

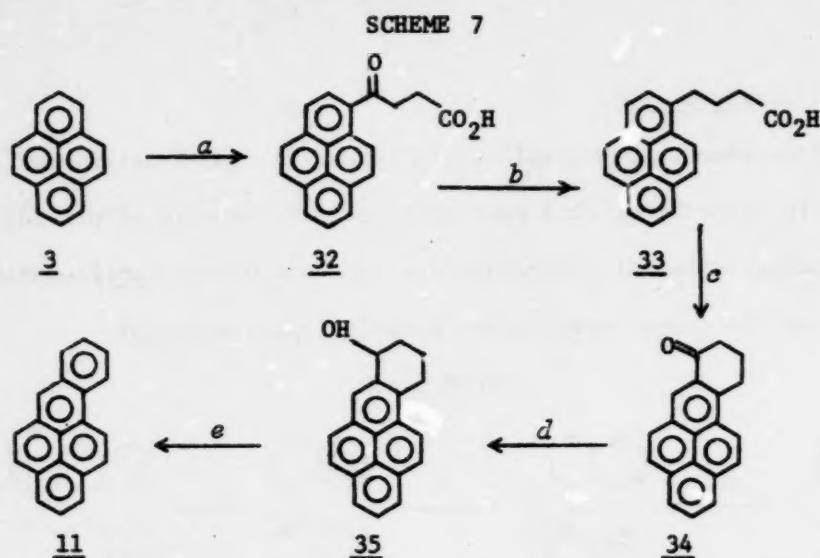


^aAl, C₆H₆, C₂H₅OH, HgCl₂. ^bCH₃CO₂H, (CH₃C)₂O. ^cMaleic anhydride, Δ . ^dPbO₂, C₁₀H₁₈, Δ . ^eQuinoline, Cu, Δ . ^fPd/C, Δ . ^gNBS, CCl₄, Δ ; CH₃CO₂Na, Δ .

A 10.4-g sample in 89 vials was supplied.

g. Benzo[a]pyrene (11)

The route shown in Scheme VII was used to prepare 11.^{21,22,23} We consider the synthesis of 11 to be troublesome. The deoxygenation of 32 to 33 is best carried out with HI-P₄;² other methods of reduction (Wolff-Kishner and Pd/C hydrogenolysis) afforded low yields of product and caused some side-chain cleavage.²² Cyclization of 33 to 34 was done in liquid HF.² PPA in this case gave poor yields of impure product.^{2,22}



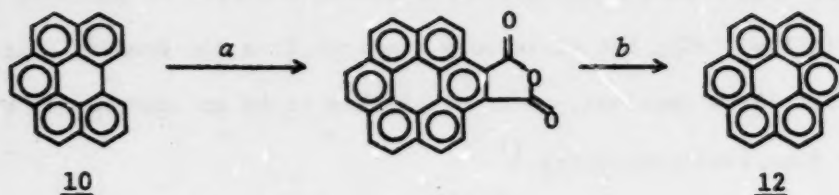
^aAlCl₃, C₆H₆, succinic anhydride. ^bHI, P₄, Δ. ^cHF. ^d(*i*bu)₂AlH, C₆H₆.
^ePd/C, Δ.

A 9.7-g sample of 11 in 41 ampoules and vials was provided.

h. Coronene (12)

This hydrocarbon is being prepared as shown in Scheme VIII. The synthesis is dependent upon the product from Scheme VI and is currently being studied.^{20,24}

SCHEME 8

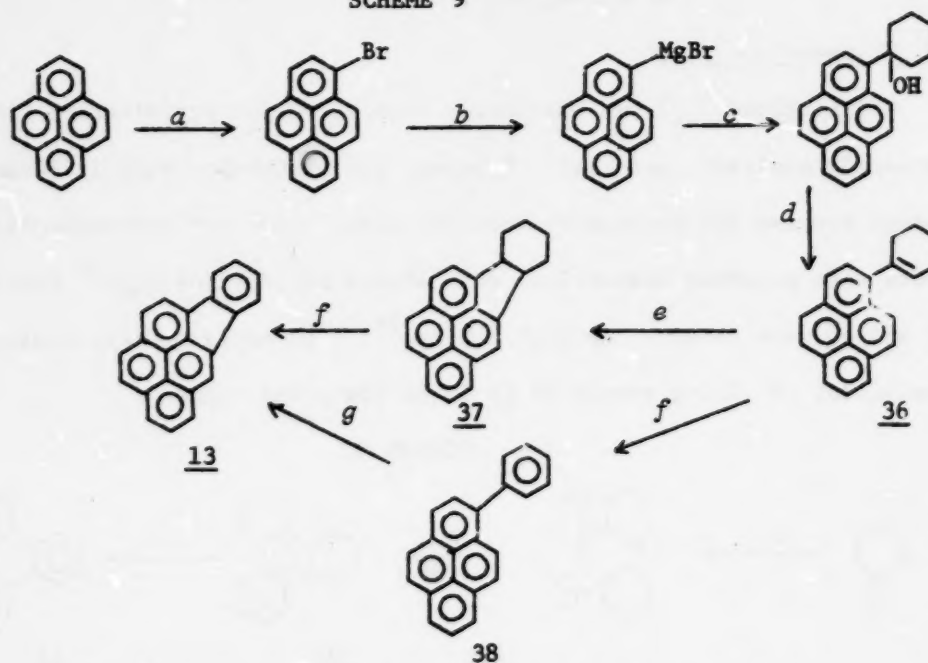


a Pd/C, Δ . b Quinoline, Cu₂O, Δ .

1. Indeno[1,2,3-cd]pyrene (13)

Hydrocarbon 13 is being prepared as shown in Scheme IX. As in Scheme VI, this route is capable of producing additional hydrocarbons -- 36, 37, and 38. We believe this synthesis²⁵ of 13 to be new and it represents a considerable improvement over earlier preparations.²⁶

SCHEME 9



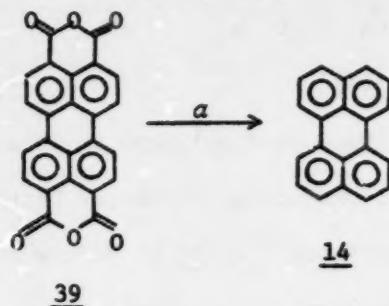
a CuBr₂, CCl₄, Δ . b Mg, ether, initiated by CH₃MgBr. c Cyclohexanone, Δ .

d Amberlyst-15, Δ . e C₆H₅Cl, Amberlyst-15, Δ . f Pd/C, Δ . g AlCl₃, NaCl, Δ .

1. Perylene (14)

The route in Scheme X appears to be new as a source of perylene (14).²⁴ The yield is low (12%), but since only one step from the commercially available material 39 is involved, we consider this to be an improvement over previously described procedures.²⁷

SCHEME 10

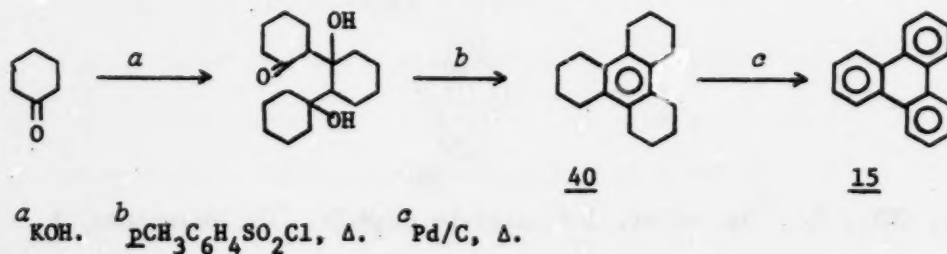


^a Quinoline, Cu₂O, Δ.

k. Triphenylene (15)

Triphenylene (15) was originally considered for purification from commercially available material. However, the synthesis route in Scheme XI showed promise and we thus avoided the usual "coal tar" contaminants. This route also provided symmetrical dodecahydrotriphenylene (40).²⁸ Since both 15 and 40 were obtained in high purity,^{29,30} we consider that synthesis was justified. A 12.3-g sample of 15 in 96 vials was supplied.

SCHEME 11



HYDROCARBONS ADDED SUBSEQUENT TO THE 1974 LIST

An alphabetical list of the 21 aromatic compounds requested by the Chemistry and Physics Laboratories, NERC, RTP, NC, and their current status is shown on page 1 (Section 1, Introduction). Subsequently benzo[c]phenanthrene (44), which has been supplied, was added to the list during the 1976 renewal at the request of the sponsor.

The structure and status of other hydrocarbons (including benzo[c]phenanthrene) currently being prepared for the Chemistry and Physics Laboratory, NERC, ATP, NC, are given below.

This group of hydrocarbons came under consideration because some occur as intermediates (27, 30, 40) in the synthesis of specific hydrocarbons or are easily obtained as a side product of a given synthesis (31). Some hydrocarbons in this group resulted in part from collaborative efforts with the American Petroleum Institute Research Project in the early phase of the work and more recent syntheses for the thermodynamic group at the ERDA station in Bartlesville, Oklahoma (27, 46, 47, 50). The preparation of the hydrocarbons in this group may be traced by reference to the specific synthesis scheme numbers shown below. Schemes XII, XIII, AND XIV, which do not appear in the earlier part of this report, are subsequent to this group of hydrocarbons.

Benzo[c]phenanthrene (44), Scheme XII below, shipped 9.7 g in 87 vials

Dibenzo[c,d]phenanthrene (31), Scheme VI (p. 19), current work

s-Dodecahydrotriphenylene (40), Scheme XI (p. 22), shipped 8.8 g in 62 vials

1,2,3,3a,4,5-Hexahydrophenanthrene (47), Scheme XIII below, current work

cis,anti-4,5,6,6a,6b,7,8,12b-Octahydrobenzo[j]fluoranthene (27),

Scheme IV (p. 18), shipped 10.3 g in 51 vials

1,2,3,4-Tetrahydroanthracene (50), Scheme XIV below, current work

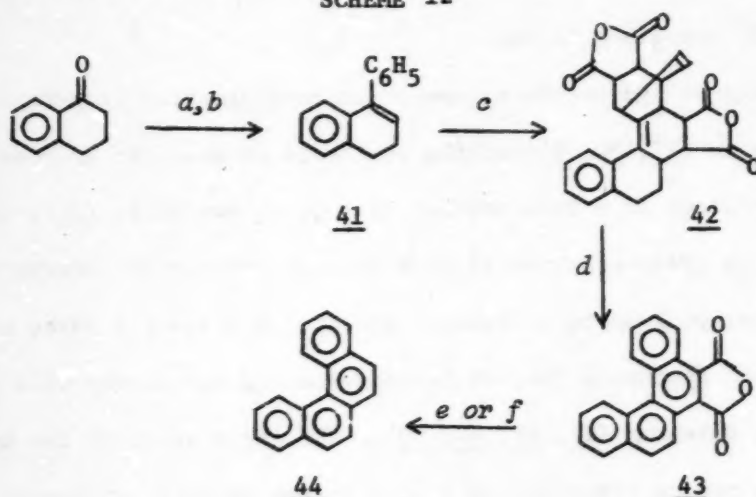
Tetrahydrodibenzo[c,d]phenanthrene (30), Scheme VI (p. 19), current work

4,5,9,10-Tetrahydropyrene (46), Scheme XIII below, current work

Benzo[c]phenanthrene (44)

Benzo[c]phenanthrene (44), added to the list in the 1976 renewal, was prepared by the procedure shown in Scheme XII. This preparation was achieved with some improvement (33% vs. 16%) over the published report.^{18,31}

SCHEME 12



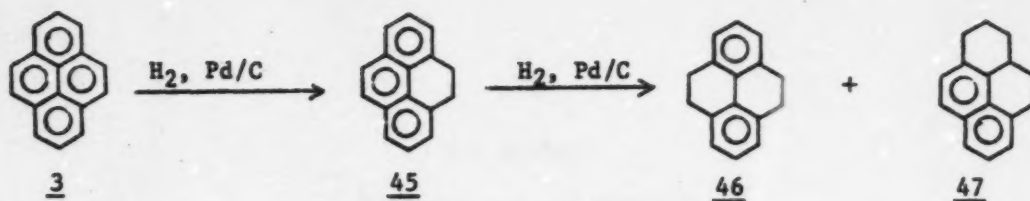
^a $\text{C}_6\text{H}_5\text{MgBr}$, ether. ^b Oxalic acid, C_6H_5 , Δ . ^c Maleic anhydride, Δ . ^d Pd/C , methylnaphthalene, Δ , or S, Δ . ^e Ba(OH)_2 , Cu, Δ . ^f Quinoline, Cu, Δ .

A 9.7-g sample of 44 in 87 vials was supplied.

Tetrahydropyrene (46) and Hexahydropyrene (47)

Hydrogenation of pyrene (3) with Pd/C in acetic acid leads to the tetrahydro and hexahydro products 46 and 47.³² The separation and purification of these hydrocarbons was achieved through use of a picric acid column, since 46 does not form a picrate whereas 47 does.⁴ Hydrocarbons 46 and 47 are currently undergoing purification.

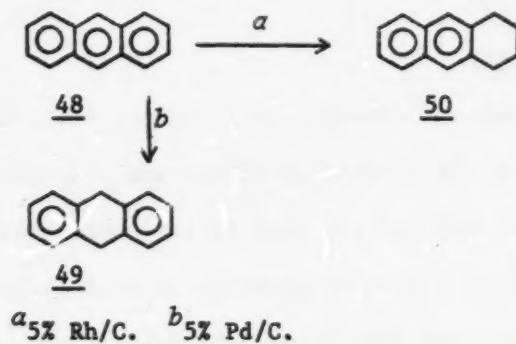
SCHEME 13



1,2,3,4-Tetrahydroanthracene (50)

Selective hydrogenation of anthracene (48) to 1,2,3,4-tetrahydroanthracene (50) is readily achieved through catalytic hydrogenation in the presence of Rh/C or Rh/Al₂O₃ to give 50, whereas Pd/C leads to 49.⁴

SCHEME 14



SECTION 5
EXPERIMENTAL PROCEDURES³³

As pointed out in Section 4, some of the synthesis steps and experimental techniques used in preparation and purification of the hydrocarbons in this report are known. However, new techniques and reagents generally provide some improvement of most syntheses and where appropriate, these are presented in this section.

Purification of Solvents

Bulk solvents (acetone, benzene, cyclohexane, ethyl ether, 95% ethyl alcohol, ethyl acetate, isohexane, isooctane and toluene) were purchased from commercial sources and redistilled from an all-glass system before use. Ethyl ether was distilled from sodium borohydride to destroy peroxides, and then stored over ferrous sulfate heptahydrate to inhibit their reformation. Acetic acid was not processed.

Depending upon the need, some solvents received additional treatment. For example, cyclohexane was repeatedly stirred with concentrated sulfuric acid until there was no visible darkening of the sulfuric acid layer. The processed cyclohexane was then separated from the sulfuric acid layer and freed of traces of sulfuric acid by filtering through basic alumina. The filtrate was then redistilled. Another approach was to percolate cyclohexane, isohexane, and isooctane through layers of alumina and silica gel.

Benzene was purified by refluxing with aluminum chloride, washing with water, drying, filtering, and distilling.

Purification of Chrysene (1), Fluoranthene (2), Pyrene (3), and 1,3,5-Tri-phenylbenzene (4).

Hydrocarbons 1, 2, 3, and 4 were obtained from commercial sources and their purification included use of the techniques described in Section, pp. 6-13. Their pmr spectra are presented as Figures 6-9 respectively.

Purification of Chrysene (1)

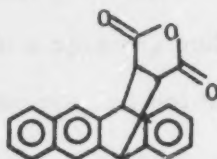
Chrysene is commercially available and consequently direct purification was used rather than synthesis. Commercial 1 has been reported to contain benzocarbozoles³⁴ and possibly other aromatic amines, which are difficult to remove. Accordingly, 50 g of 1, which had already received a purification treatment with picric acid,² was placed in a Soxhlet extraction apparatus (see Figure 2) containing a 3" layer of Kaolin coated with ferric chloride.³⁵ Chrysene was then extracted through the Kaolin layer with isohexane. As expected, an indigo coloration developed which indicated the presence of aromatic amine. An 0.5% impurity remained. This impurity was removed through repeated recrystallization from benzene to yield 17.5 g of colorless crystals. The final purification was then affected by sublimation, cf. Figure 3, and a 10.6-g sample, mp 251-253°, contained in 94 vials, was supplied. The purified chrysene was not sufficiently soluble to permit obtaining a conventional 100 MHz pmr spectrum, and therefore a Fourier-transform spectrum (Figure 6) was obtained. As a consequence, spurious peaks from solvent impurities appear in the spectrum in the nonintegrated region.

Purification of Fluoranthene (2)

Fluoranthene was routinely purified using recrystallization and picrate purification techniques.² Since a larger sample was required for API use as well, zone refining was used in the final purification stage to give 2, mp 110-111°. The pmr spectrum is shown in Figure 7.

Purification of Pyrene (3) and 1,3,5-Triphenylbenzene (4)

Tetracene is a frequently cited impurity in commercial pyrene. Accordingly, we treated the impure pyrene with maleic anhydride dissolved in boiling toluene to remove this impurity. The resulting Diel's-Alder product³⁶ of tetracene shown below is then selectively removed by adsorption on basic alumina. Pyrene is unaffected by maleic anhydride. The subsequent purification, including recrystallizing and zone refining, gave 3, mp 155-156°.



1,3,5-Triphenyl benzene (4) was purified by recrystallizing from hot isopropyl alcohol and then leaching with hot isooctane. It was then eluted through acidic alumina, contained in a Soxhlet, with isohexane.³ The vacuum-dried product melted at 174-175°. The pmr spectra of 3 and 4 are in Fig. 8 and 9 respectively.

Synthesis and Purification of Anthanthrene (5, Scheme I) Dibenzo[def,mno]-chrysene.

Anthanthrene (5) was synthesized as shown in Scheme I and as described.^{8a,b} Since 5 is typical of high-molecular-weight polycyclic aromatic hydrocarbons, a description of its purification is pertinent. Crude 5 from dehydrogenation was eluted through a Dicalite column in a Soxhlet column (Fig. 2) with toluene to remove catalyst. After recrystallization from toluene, no starting material, 21, was detectable. The sample was further recrystallized from toluene and then eluted through neutral and basic alumina columns. A picrate was prepared, recrystallized from toluene, and cleaved.² The final purification of 5 included recrystallizing from toluene, boiling with hot isohexane³⁷ to

remove toluene and then pumping at 0.1-mm for 2 days at room temperature, 2 days at 70° and 1 day at 120°. Anthanthrene was gold-colored and the mp was 264-265.5°. The purified 5 was transferred to ampoules and screw-cap vials in a nitrogen atmosphere. The ampoules were then evacuated and sealed.

This hydrocarbon was not sufficiently soluble to obtain a satisfactory pmr spectrum.

Synthesis and Purification of Benz[a]anthracene (6, Scheme II)

Our synthesis⁹ of 6, mp 140-142°, has been published.¹⁰ The final recrystallization was from ethanol and the pmr spectrum is shown in Fig. 10.

Synthesis and Purification of Benzo[b]fluoranthene (7, Scheme III)

A 160-g sample of fluorene was dissolved in 1.7 l. of xylene containing 16.6 g. of KOH. To this mixture was added 140 g of freshly distilled o-chlorobenzaldehyde and one drop of piperidine. The mixture was heated to reflux with stirring and the water that evolved from the reaction was collected in a Dean-Stark trap. After the formation of water ceased, the reaction mixture was cooled, poured into water, and extracted with toluene. The extract was washed with dilute HCl, water, aqueous sodium carbonate, and again with water. After drying (MgSO₄) and filtering, toluene and xylene were removed by vacuum-distillation to give 263 g (91%) of an orange oil consisting mainly of 24. This oil was used in the cyclization reaction without purification. The preparation of 24 was repeated several times with different amounts of starting materials. One run was made using N-phenyltrimethylammonium hydroxide as the basic catalyst. The yield from this run approximated that of the other runs.

To cyclize 24, 352 g (1.2 mol) was mixed with 1 l. of technical grade quinoline and 141 g of KOH. This mixture was heated under a nitrogen atmosphere at reflux temperature for 2 hr. Water evolved from the reaction

and was collected in a Dean-Stark trap. When water no longer formed, the reaction mixture was cooled and acidified with 4 l. of conc. HCl. The solution was extracted with benzene (3 x 3 l.) and the combined benzene layers were washed with water. This extract was passed through basic alumina 3 times to remove black tarry impurities. The red filtrate was then concentrated to 237 g. (78%) of orange solid containing 7. After two recrystallizations from ethanol and one from benzene, 7 was obtained as a faint yellow solid. The yield at this point was 50%. Further purification yielded a white solid with a faint yellow tint, mp 167° to 168° [lit.¹³ 167°]; ir spectrum (KBr) 890, 772, 737, 731 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 252, M^+ (100), 251 (06), 250 (17), 248 (05), 126 (15), 125 (09).

Synthesis and Purification of cis,anti-4,5,6,6a,6b,7,8,12b-Octahydrobenzo-[j]-fluoranthene (27, Scheme IV) and Benzo[j]fluoranthene (8, Scheme IV).

1-Tetralone was reduced to 1-tetralol by treatment with 4.4 equivalents of diisobutylaluminum hydride in toluene solvent. After all of the 1-tetralone had been added to the reducing agent, the mixture was stirred for an additional 0.5 hr. Ethyl acetate was added to decompose the excess reducing agent. The reaction mixture was then cautiously poured on ice containing conc. HCl. This addition was done cautiously, since there is considerable evolution of isobutane and frothing can cause loss of material. The acidified reaction product was then transferred to a separatory funnel and the toluene layer was washed with water, a saturated solution of sodium carbonate, and then again with water. The extract was filtered through solid sodium carbonate, dried (MgSO_4), filtered, and concentrated by rotary evaporation under vacuum to yield 86% of crude 1-tetralol.

Tetralol (516 g) was dehydrated by steam distillation from 20 g of oxalic acid. The steam condensate and the dihydronaphthalene were separated; the organic material was dried (MgSO_4) and distilled at 70° (0.8 mm) to yield 80% (362 g, 2.8 mol) of 1,2-dihydronaphthalene.

1,2-Dihydronaphthalene (108 g, 0.83 mol) in a 1-l. fluted flask equipped with mechanical stirrer and condenser containing 500 ml of benzene and 20 g of A-15 resin was heated at reflux for 25 hr. The solution was cooled, filtered to remove resin and concentrated by rotary evaporation. The residue was distilled in a Kugelrohr apparatus at 170° (1 mm) and yielded 77 g of crude dimer³⁸ consisting of a mixture of 25, 26, and 27. Crystallization from an ether:isohexane mixture (1:1) gave 18 g of colorless crystals, mp $85-88^\circ$, consisting mainly of 27. Recrystallization of this product from ether and also from acetone gave colorless crystals of 27, mp $92-93^\circ$ [lit.¹⁵ 93°]; mass spectrum (70 eV) m/e (rel intensity) 260 (100), 259 (31), 232 (44), 217 (35), 169 (61), 78 (44).

The mother liquor remaining from the purification of 27 and the other components of the original cyclization mixture were dehydrogenated by heat in the presence of 10% Pd/C under a nitrogen atmosphere for 3 hr at 230° . The reaction mixture was then cooled to 100° and toluene was added. The reaction mixture was then cooled to room temperature and filtered through Dicalite to remove catalyst. After concentration by rotary evaporation, the brown residue was triturated with isohexane to give yellow crystals of 8 mixed with 28. Our attempts to separate 8 and 28 were not successful, and therefore we repeated the dehydrogenation, using material which did not contain 25. This latter dehydrogenation gave bright yellow crystals of 8 in practically quantitative yield and free of 28. The purification of 8 was accomplished through use of a picric acid column.⁴

The final purification of 8 involved elution through alumina with isohexane, concentration to remove solvent, recrystallization from ethanol and sublimation at 90° (0.1 mm), to give 8, mp 164-165°; mass spectrum (70 eV) m/e (rel intensity) 252 (100), 251 (7), 250 (20), 126 (7), 57 (8), 43 (8).

Synthesis and Purification of Benzo[k]fluoranthene (9, Scheme V)

A solution of acenaphthenequinone (72.5 g, 0.4 mol) o-phenylenediacetonitrile (67 g, 0.43 mol), and 1100 ml of piperidine was placed in an ice bath for 50 min without stirring, stirring for 40 min at ice bath temperature and then stirring for 4 hr at ambient temperature. After 65 hr, the reaction mixture was treated with 8.6 l. of 5% hydrochloric acid and filtered. The filter cake was washed with water, recrystallized from nitrobenzene, and leached with isohexane to yield 88.5 g (73.6%) of 7,12-dicyanobenzo[k]fluoranthene (29): mp 357-359°.

A mixture of 30 g (0.1 mol) of 29 and 3000 g of 100% phosphoric acid was stirred for 21 hr at room temperature, heated to 280° for 18 hr and then cooled to room temperature. The reaction mixture was then poured into 2 l. of water, stirred overnight, and extracted with benzene. The benzene extract was concentrated, the resulting yellow solid was collected by filtration, placed in a Soxhlet apparatus over a bed of alumina and then extracted with isohexane.³ The isohexane solution was concentrated, yielding 20.5 g (81.3%) of 9: mp 217-217.3° [lit.¹⁷ 217-217.4°]; mass spectrum (70 eV) m/e (rel intensity) 253 [(M + 1)⁺ 6], 252 (100), 126 (4), 113 (1), 58 (1).

Synthesis and Purification of Benzo[ghi]perylene (10, Scheme VI)

The synthesis of 10 is an adaptation of a published procedure.¹⁹

The diol and the corresponding diene shown in Scheme 6 were prepared as

follows: 1-Tetralone (146 g, 1.0 mol) and 5.1 g of mercuric chloride were added to a 3-l., 2-neck, round-bottom flask (equipped with nitrogen inlet, reflux condenser, magnetic stirring, and heating mantle) containing 1400 ml of anhydrous benzene, 100 ml of anhydrous ethanol and 51.4 g (2 g. atom) of aluminum foil. The system was flushed with nitrogen and then brought to reflux. After 20 hr, the liquid contents were decanted and washed twice with cold 10% HCl, and then with water. The organic phase was dried (MgSO_4), filtered, and concentrated through rotary evaporation. The resulting diol was then dissolved in a mixture of 300 ml of acetic acid and 300 ml of acetic anhydride. This solution was heated at reflux for 5 hr and then concentrated under vacuum to give 38 g (68%) of the diene, mp 135-137.5°, shown in Scheme VI.

The diene product from above was then treated with 10 molar equivalents of maleic anhydride at 120° for 8 hr, to give the Diels-Alder product shown in Scheme VI. This adduct was isolated by dissolving the cooled reaction mixture in hot acetic acid, from which it crystallized to give 163 g (84%) of material, mp 234-252°.

The conversion of this Diels-Alder product to 10 was accomplished by heating 3.57 g (0.10 mol) at 265° for 13 hr in the presence of 0.8 g of 10% Pd/C in a stream of nitrogen. Heating was discontinued at this time because CO_2 could no longer be detected in the effluent nitrogen. Purification of 10 was accomplished by elution from basic alumina in a Soxhlet extractor³ with hot benzene. This procedure yielded 2.24 g (80.5%) of 10. Recrystallization from benzene and sublimation at 260° (0.02 mm) gave purified 10 as yellow crystals, mp 276-277°C [lit.¹⁹ 273°]. Further handling during filling of vials was done in an argon atmosphere.

Synthesis and Purification of Benzo[a]pyrene (11, Scheme VII)

The synthesis shown in Scheme VII follows a reported route.²¹ In repeating this synthesis, we experienced difficulty in the conversion of 32 to 33 as well as 33 to 34, since procedures used previously failed to give satisfactory results. From this work we have selected the following. A sample (25 g, 0.09 mol) of the keto acid 32, red phosphorus (11 g), 57% HI (20 ml), and acetic acid (400 ml) were heated under a nitrogen atmosphere for 96 hr. The warm reaction mixture was filtered and then diluted with water (1.5 l.), whereupon acid 33 separated as a solid precipitate. This solid was collected by filtration, washed with 1 l. of water and then dissolved in 200 ml of saturated sodium bicarbonate solution. The solution was filtered and reprecipitated by acidification with 10% HCl. Recrystallization from toluene-isohehexane gave 17 g (0.07 mol, 72%) of colorless plates of 33, mp 187-188°C [lit.²¹ 187-188°C]; ir (KBr) cm^{-1} 3010, 2940, 1690, 1460, 1430, 1335, 1320, 1275, 1210, 910, 820, 755, 725, and 710; mass spectrum (70 eV) m/e (rel intensity) 288 (M^+ , 30), 228 (16), 227 (17), 216 (20), 215 (100), and 213 (23); pmr (DMSO- d_6) δ 8.49-7.94 (m, 9, ArH), 3.38 (t, 2, ArCH₂, J=7 Hz), 2.44 (t, 2, CH₂CO₂H, J=6 Hz), and 2.05 (pentet, 2, ArCH₂CH₂, J=7 Hz).

The acid 33 (25 g, 0.09 mol) was cyclized to ketone 34 by adding small portions over a 30-min. period to 200 g (10 mol) of anhydrous liquid HF contained in polyethylene bottle. During the addition, the bottle was cooled in ice. After a few min., ice was removed and nitrogen was swept through the sample to evaporate HF, which was trapped by bubbling through water and then alkali. After the HF had evaporated, the product mixture was broken up and triturated with saturated K₂CO₃ and then filtered. The filter

cake (22 g, 0.80 mol) was then purified by extraction with ethanol in a Soxhlet apparatus containing 100 g of neutral alumina. The ethanol extract yielded 86% (20 g, 0.07 mol) of ketone 34 as shiny yellow plates, mp 171-173°C [lit.²¹ 170-173°C]. The ketone 34 was converted to benzo[a]pyrene (11) by reducing to the alcohol 35, dehydrating and then dehydrogenating. These steps were as follows: the ketone 34 (27 g, 0.1 mol) was dissolved in 1 l. of toluene and then added to a solution of 23 g (0.15 mol) of diisobutylaluminum hydride in 500 ml of toluene. During the addition the temperature was held below 50°. The excess reducing agent was consumed with 10 ml of ethyl acetate. The reaction mixture was then cooled and poured onto 2 kg of ice containing 250 ml of conc. HCl. The toluene layer was separated, washed with sodium bicarbonate solution and then with water. It was next dried (MgSO₄), filtered, and concentrated, to give a pale brown solid (25 g, 0.09 mol, 90%). This product was a mixture of the alcohol 35 and the corresponding alkene. Our efforts to prepare pure 35 were not successful. The crude alcohol 35 (10 g, 0.04 mol) was then dehydrated in a mixture of acetic acid (500 ml) and conc. HCl (0.5 ml) by heating at reflux for 5 min. The reaction mixture was then filtered, poured into ice water, whereupon pale yellow crystals of the alkene separated (8.2 g, 0.03 mol, 86%), mp 145-146°. This product was recrystallized from isohexane³⁷ to give 7.5 g (0.03 mol) of pale yellow plates, mp 148-149° [lit.²¹ 148-149°].

The purified alkene (18 g, 0.07 mol) was mixed with 1.8 g of 10% Pd/C and then heated in a stream of nitrogen at 320-330° for 2 hr. The flask was allowed to cool and the contents, including material which had sublimed into the neck of the flask, were transferred with hot benzene to a Soxhlet apparatus containing 80 g of neutral alumina.³ Extraction with benzene and concentration under vacuum gave a 96% yield (17 g, 0.07 mol) of crude 11. This

material was then extracted³ through 100 g of neutral alumina with isohexane to give 14 g (0.06 mol) of 11, mp 177-178°. Additional purification was accomplished by recrystallizing from toluene-isohexane. The melting point of the sublimed product was found to be 177.5-178° [lit.²¹ 176.5-177°]. The yield of the final product was 60% (11 g, 0.04 mol).

Syntheses of Coronene (12, Scheme VIII), Indeno[1,2,3-cd]pyrene (13, Scheme IX), and Perylene (14, Scheme X).

Hydrocarbons 12, 13, and 14 are currently being synthesized as shown in Schemes VIII, IX, and X respectively.

Synthesis and Purification of Triphenylene (15, Scheme XI) and s-Dodecahydrotriphenylene (40, Scheme XI)

Distilled cyclohexanone (350 g) was placed in a 2-l., round-bottomed flask fitted with a mechanical stirrer. Sodium hydroxide flakes (85 g) was added and the mixture was stirred for 72 hr. During this time the mixture turned from colorless to yellow to white with the formation of a solid product. When the reaction was stopped, the mixture was poured over 2 kg of ice and then stirred. The product (300 g) was filtered off. The filtrate containing unreacted cyclohexanone was extracted with petroleum ether and the organic layer, after separation, was washed with water and dried (MgSO₄) and filtered. Evaporation of the solvent yielded about 400 g of unreacted cyclohexanone. Yield of trimeric product was 35% (67% based on recovered cyclohexanone). Repetition in a nitrogen atmosphere caused no significant increase in the yield. A cleaner product was obtained when the crude reaction mixture was diluted with ethanol and water and then filtered. The recovery of the unreacted cyclohexanone, however, was more difficult in this case. The crude product (mp 175-188°) was recrystallized from isopropyl alcohol to give crystals of trimer; mp 181-185° (lit.^{28a} 175°; lit.^{28b} 210°);

mass spectrum m/e (rel intensity) 294 (M^+ , 4), 258 (91), 215 (142), 131 (96), 77 (125), 55 (111); ir (KBr) 3220, 2920, 2850, 1440, 1225, 1093, 950, and 825 cm^{-1} .

The cyclohexanone trimer (50 g) was dissolved in 500 ml of pyridine in a 1-l., round-bottomed flask. Benzoyl chloride (50 ml) was added and the mixture stirred at 80°C for one hr using a magnetic stirrer. The clear brown solution was cooled and then poured into 1 l. of water and the solution acidified with concentrated HCl. The product was then extracted with benzene three times and the combined benzene extracts were washed with sodium bicarbonate solution and then with water. After drying (MgSO_4) and filtering, the solvent was evaporated to a brown oil (44 g, theoretical yield). This oil was used in the next step without purification. Other acidic reagents (*p*-toluenesulfonyl chloride and A-15) were equally effective.

A 44-g sample of dehydrated material (prepared using benzoyl chloride in pyridine) was heated in a fused salt bath at 350°C under nitrogen for 90 min. Water was eliminated. The flask was cooled, the solidified mass was then washed with small amounts of methanol in order to remove unreacted material. The residue, weighing 39 g (89% yield) was passed through alumina and 36.5 g (89% yield) of a white crystalline dodecahydrotriphenylene (40); mp 228–230°C (lit.^{28a} 232°); mass spectrum (70 eV) m/e (rel intensity) 240 (M^+ , 1641), 212 (538), 211 (401), 199 (497), 198 (572), and 183 (430); pmr (CDCl_3) δ 1.60–1.96 (broad singlet, all nonbenzylic protons) and δ 2.38–2.74 (broad singlet, all benzylic protons).

The crude 40 was passed through alumina in a Soxhlet column using isohexane as the refluxing solvent. Following this, the material was recrystallized three times from benzene-isohexane mixture. This procedure removed

traces of oily impurities resulting from the pyrolysis. Some solvent was retained in the crystals, even after extensive pumping. The compound was found to be devoid of detectable impurities (by glc) at this stage. A final sublimation procedure was adopted in order to remove the solvent and to improve the purity of the compound. A special apparatus shown in Fig. 3 was constructed for this purpose.

The sublimed compound condensed on the stem above the level of the fused salt. When the major portion of the compound had sublimed, the material was scraped out and sealed in oven-baked, previously weighed vials.

Combustion calorimetry by the Thermodynamics Research Group at the Bartlesville ERDA station showed 40 to be 99.987%.

A 15-g sample of 40 and 1.5 g of 10% Pd/C were heated in a round-bottomed flask immersed in a fused sodium nitrite-sodium nitrate bath. Hydrogen gas started bubbling out (attached bubble tube) when the temperature reached 300°C. The flask was heated at this temperature for two hours until no more hydrogen evolved. The flask was cooled and the hard residue was dissolved in benzene and the suspended Pd/C catalyst was removed by filtering through Dicalite. Evaporation of the solvent gave a quantitative yield of 15. The course of the reaction could be followed by glc which showed the starting material giving rise to three other peaks and one of the peaks remaining at the end of the reaction. Attempts to stop the reaction after the formation of a partly aromatized product were unsuccessful, since the reaction always yielded a mixture of products, the ratio varying with time.

Crude 15, obtained by dehydrogenation of 40, was almost free of starting material and any of the partly dehydrogenated products. Hydrocarbon 15 was further purified by Soxhlet extraction through alumina,³ recrystallization from benzene-isohexane, and picrate formation and recrystallization followed

by decomposition of the picrate.² The final step was sublimation to remove trapped solvent. This gave colorless 15:³⁰ mp 195-197°C (lit.^{28c} 199°C); mass spectrum (70 eV) m/e (rel intensity) 229 [(M + 1)⁺, 818], 228 (M⁺, 3878), 227 (435), 114 (443), 113 (496), and 112 (214); pmr (CDCl₃) δ 7.54-7.74 (multiplet protons) on C-1, C-4, C-5, C-8, C-9, C-12), 8.54-8.74 (multiplet protons on C-2, C-3, C-6, C-7, C-10, C-11.)

Synthesis and Purification of Benzo[c]phenanthrene (44, Scheme XII)¹⁸

A solution of 1-tetralone (505 g, 3.46 mol) and 500 ml of anhydrous ether was added to an ether solution of 5.1 mol of phenyl magnesium bromide at such a rate as to maintain reflux. After addition, reflux was maintained for 1 hr. The reaction mixture was then poured onto an excess of ice cold 10% hydrochloric acid and then steam distilled to remove volatile materials. The pot residue was extracted with ether, the ether extract was concentrated and the resulting liquid was dissolved in 1 l. of benzene containing 5 g of oxalic acid. Water was removed by azeotropic distillation. The benzene solution was concentrated, passed through basic alumina, and vacuum-distilled to yield 445 g (62%) of 1-phenyl-3,4-dihydronaphthalene (41); bp 135-140° (2 mm); ir (neat) 3.37, 3.48, 3.60, 6.00, 6.31, 6.79, 7.00, 7.61, 7.85, 8.71, 9.10, 9.39, 9.82, 10.56, 11.14, 12.21, 13.08, 13.27, 13.64, and 14.39 μ , nmr (CDCl₃, TMS) δ 7.60-6.94 (m, 9, ArH), 6.14-5.92 (t, 1, C=CH), 2.78-2.10 (m, 4, CH₂).

A 93-g (0.5-mol) sample of 41 and maleic anhydride (233 g, 2.38 mol) were mixed and heated to 190° for 19 hr. The resulting oil solidified and was recrystallized from acetic acid yielding 73 g (50%) of the bis Diels-Alder adduct 42: mp 315-316° [lit.³¹ 315-316°]; ir (KBr) 3.34, 3.51, 5.90, 6.19, 6.46, 7.02, 8.00, 8.24, 10.95, 11.68, and 12.91 μ .

The Diels-Alder adduct 42 (100 g, 0.34 mol) was mixed with 5 g of 5% Pd/C in 1000 ml of 2-methylnaphthalene and then heated at reflux for 8 hr. The 2-methylnaphthalene was vacuum-distilled and the resulting solid was extracted in a Soxhlet apparatus³ with benzene to yield 74.9 g (95%) of benzo[3,4]phenanthrene-1,2-dicarboxylic acid anhydride (43); mp 249-251° [lit.³¹ 257-258°]; ir (KBr) 5.52, 5.78, 6.79, 7.16, 7.59, 7.91, 8.42, 8.80, 11.11, 11.39, 12.00, 12.42, 12.69, and 13.43 μ .

A mixture of cuprous oxide (1.52 g, 0.011 mol), 43 (3.18 g, 0.11 mol), and 50 ml of quinoline was refluxed under nitrogen for 4 hr, cooled, and poured into 500 ml of 10% hydrochloric acid, and extracted with ether. The ether solution was concentrated, dissolved in benzene, passed through basic alumina, and the benzene solution concentrated to yield 1.8 g (72%) of benzo[c]phenanthrene (44); mp 67.5-68°; ir (KBr) 3.41, 7.20, 8.32, 9.85, 10.73, 11.62, 12.20, 12.50, 13.73, and 15.35 μ ; nmr (CDCl₃, TMS) δ 9.16-9.01 (m, 2, peri-H), 8.00-7.50 (m, 10, ArH).

Synthesis of Tetrahydropyrene (46), Hexahydropyrene (47), and 1,2,3,4-Tetrahydroanthracene (50)

Hydrocarbons 46, 47, and 50 are currently being synthesized as shown in Scheme XIII and XIV.

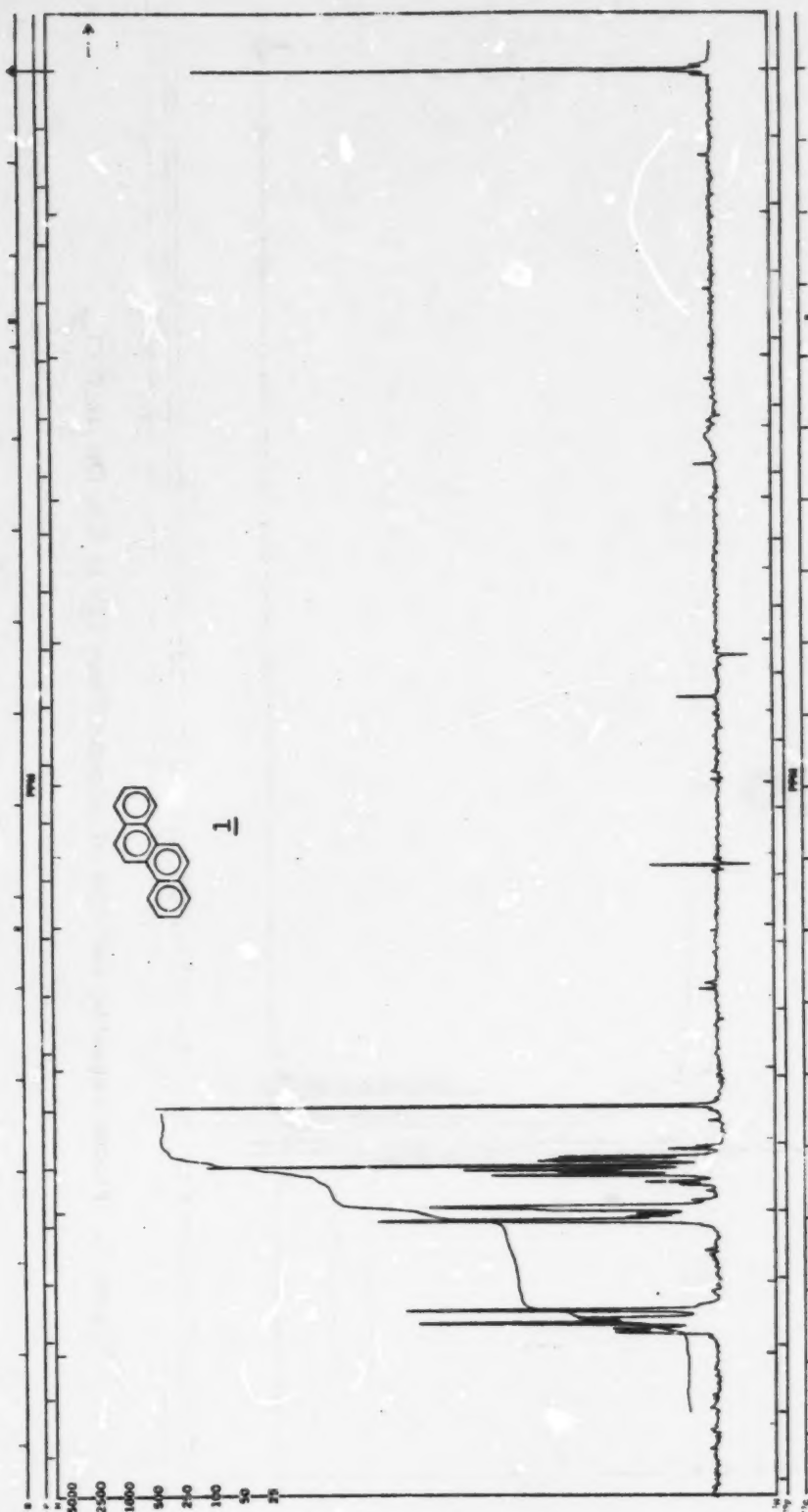


Figure 6. PMR Fourier transform spectrum of chrysene (1) in CDCl₃ at 100 MHz. Peaks in nonintegrated portion result from solvent impurities.

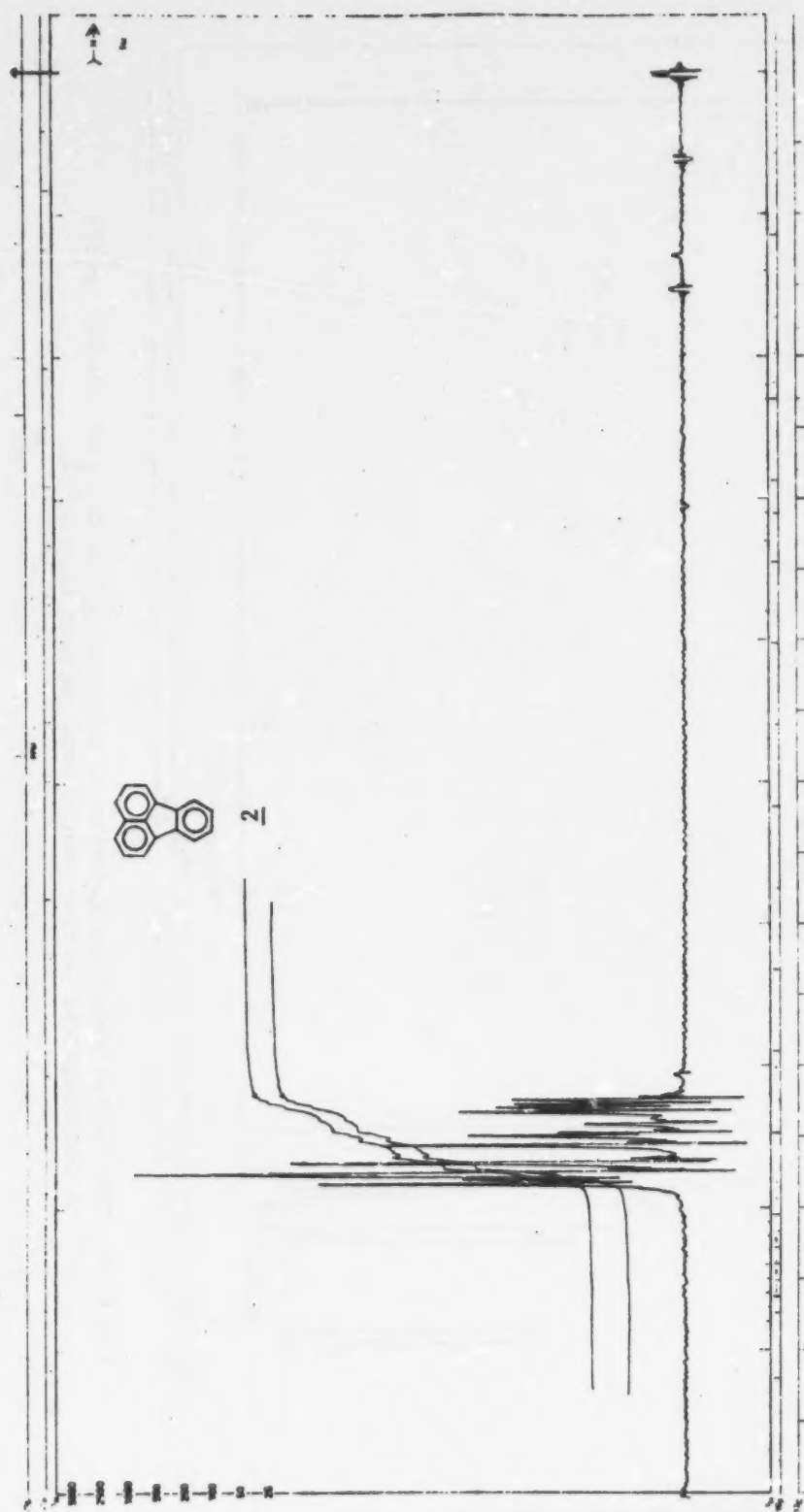


Figure 7. Proton magnetic spectrum of fluoranthene (2) at 100 MHz in CDCl₃.

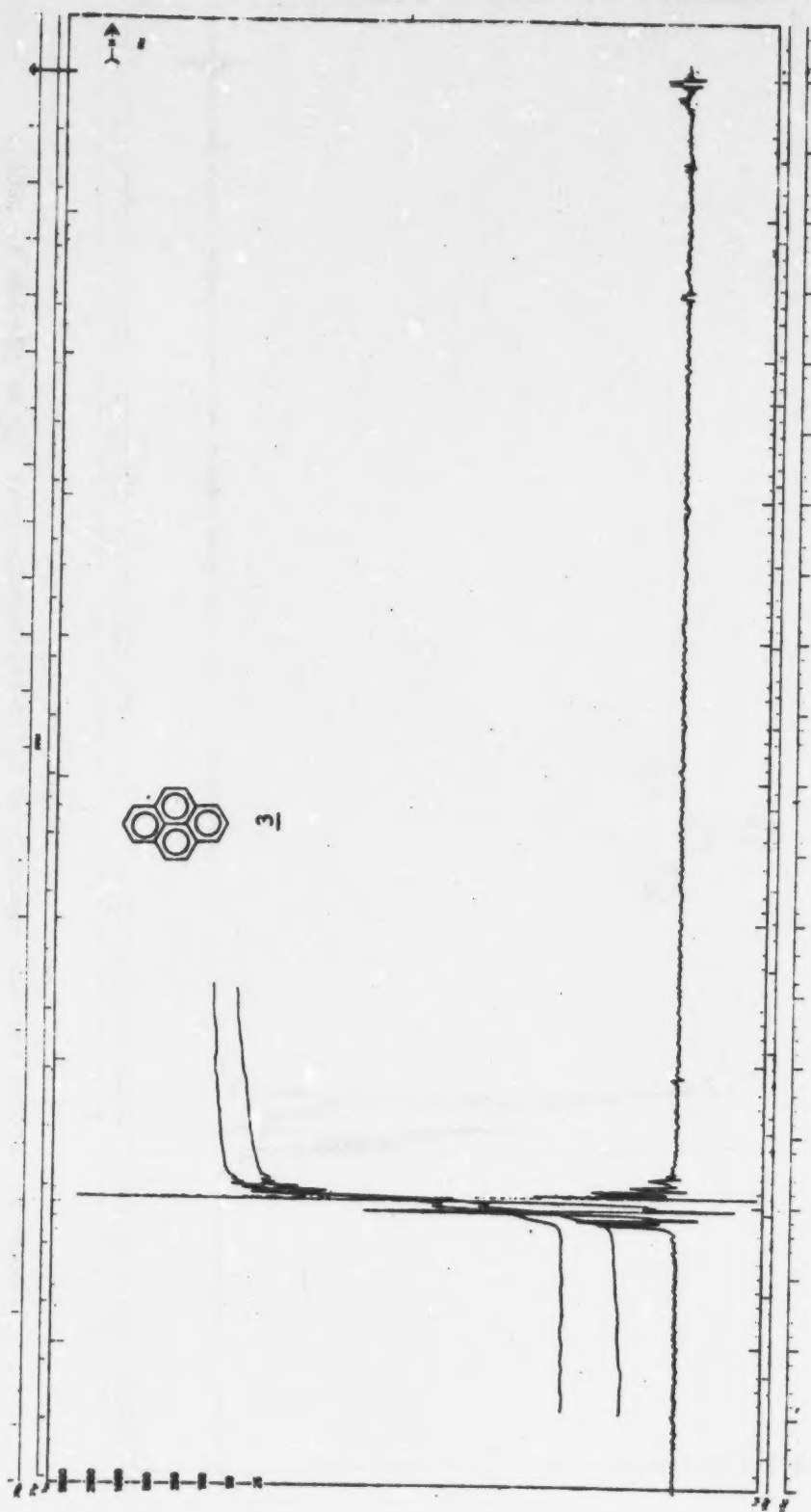


Figure 8. Proton Magnetic spectrum of pyrene (3) at 100 MHz in CDCl₃.

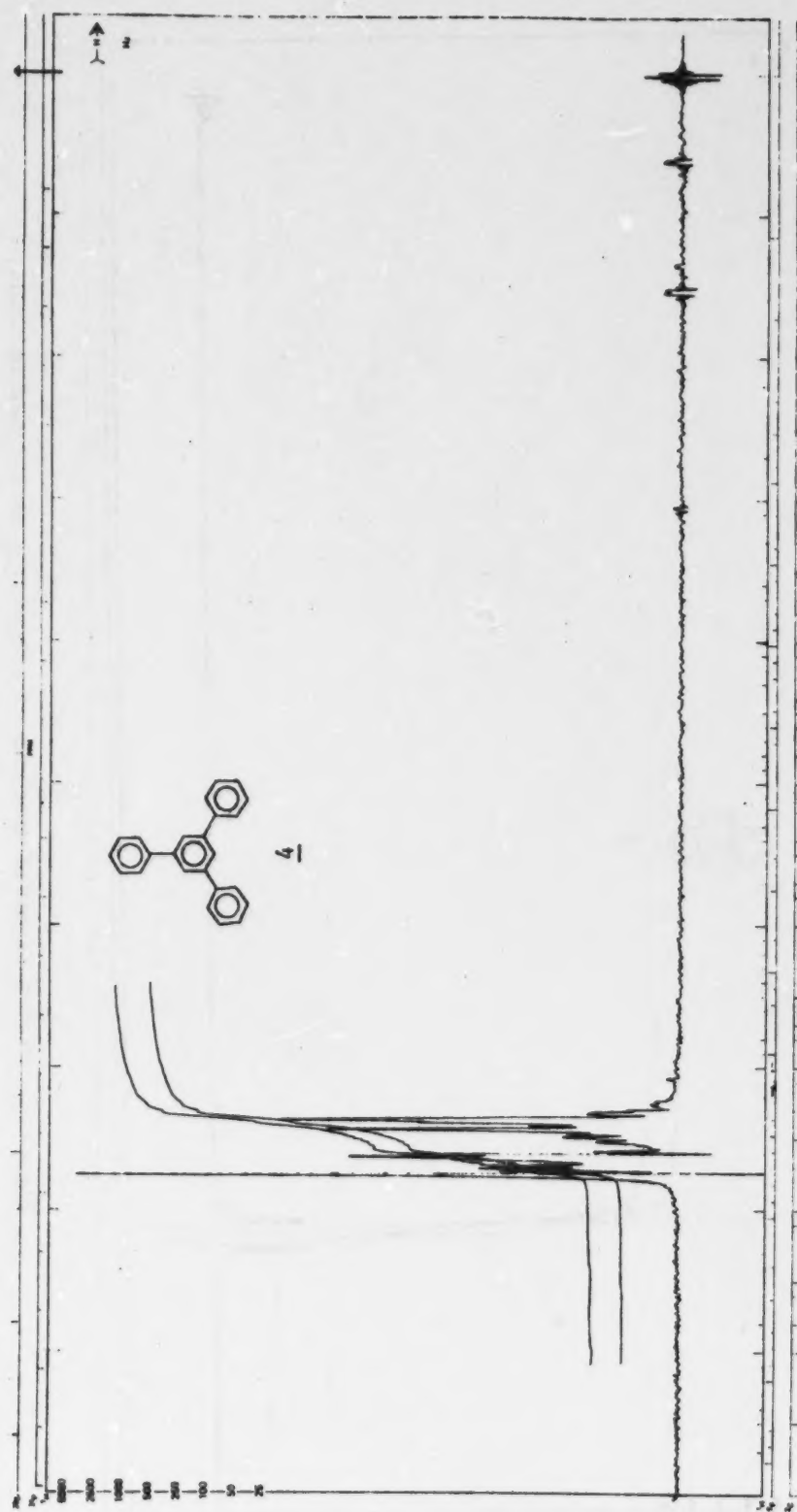


Figure 9. Proton magnetic spectrum of 1,3,5-triphenylbenzene (4) at 100 MHz in CDCl₃.

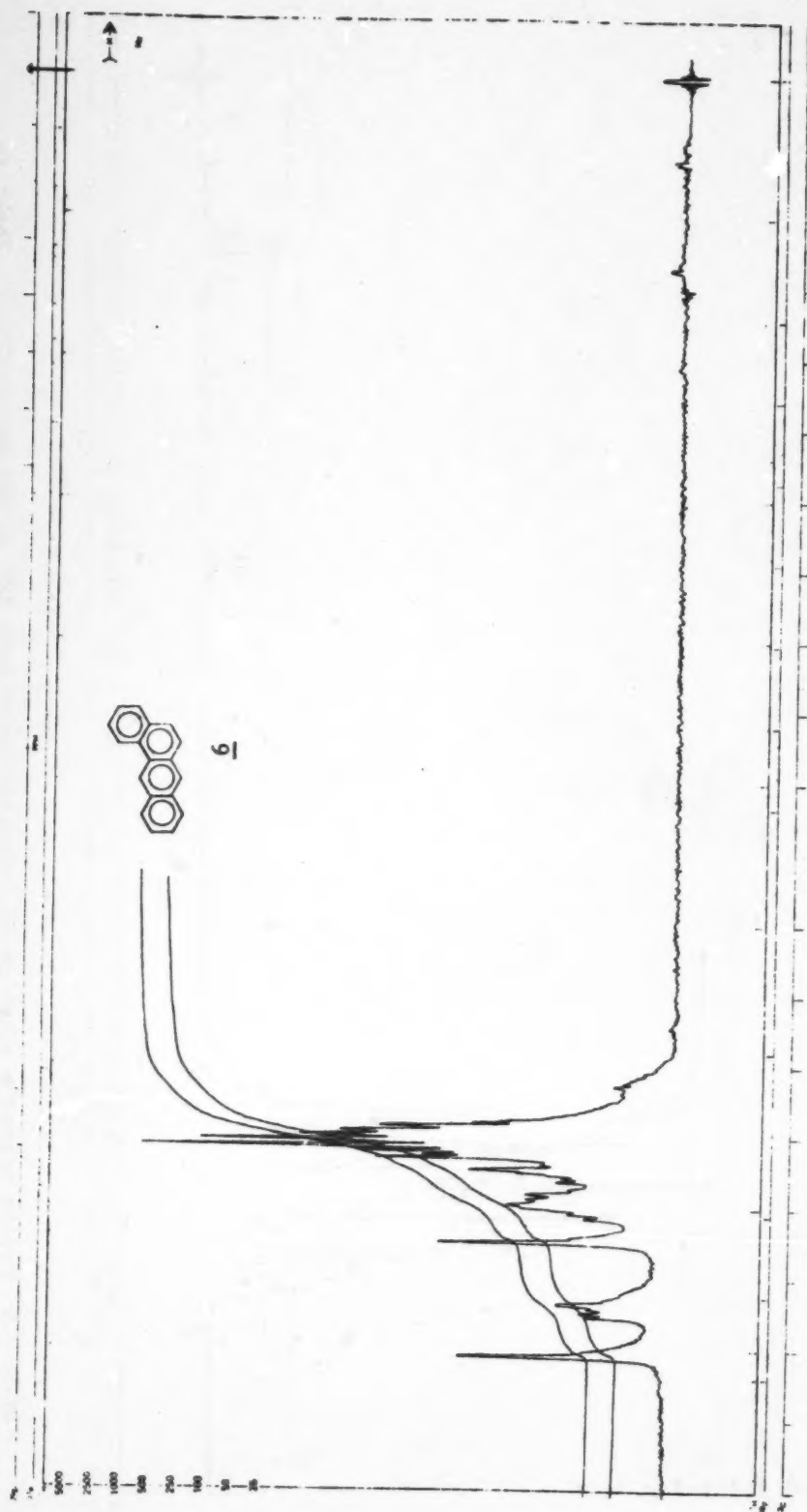


Figure 10. Proton magnetic spectrum of benz[a]anthracene (6) at 100 MHz in CDCl₃.

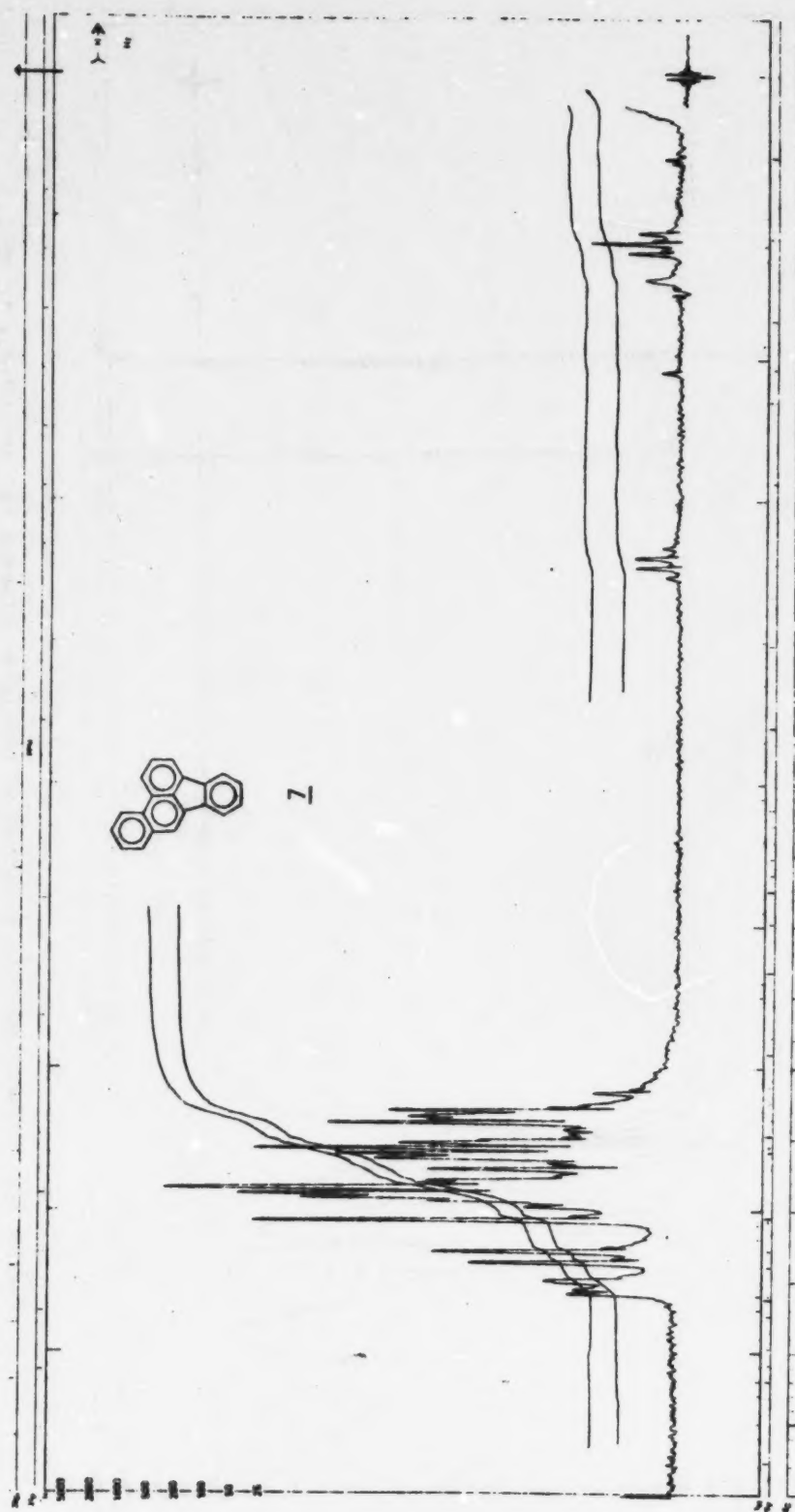


Figure 11. Proton magnetic spectrum of benzo[b]fluoranthene (7) at 100 MHz in CDCl₃. Peaks in the nonaromatic portion of the spectrum result from solvent impurities.

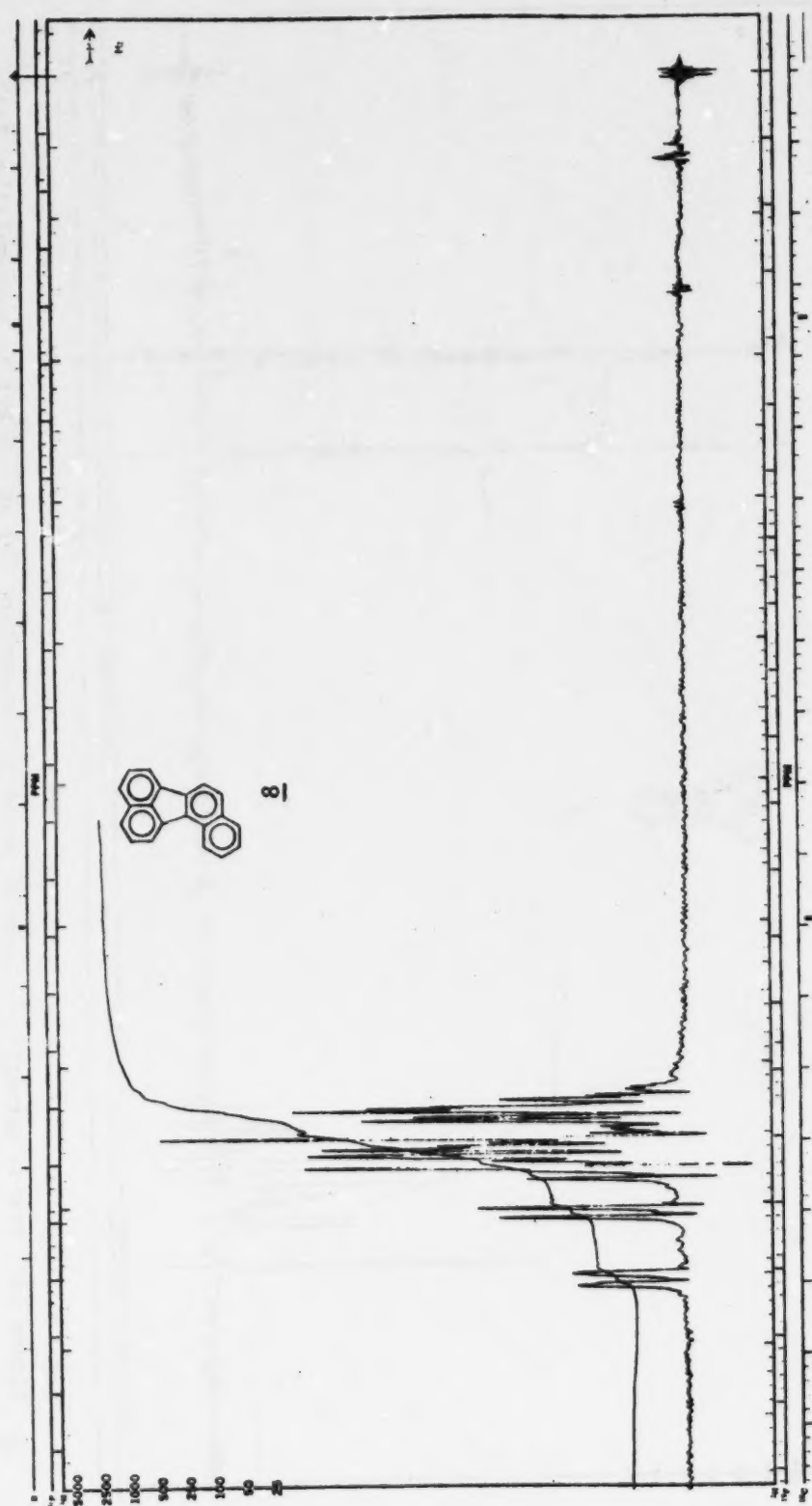


Figure 12. Proton magnetic spectrum of benzo[1]fluoranthene (8) at 100 MHz in CDCl_3 .

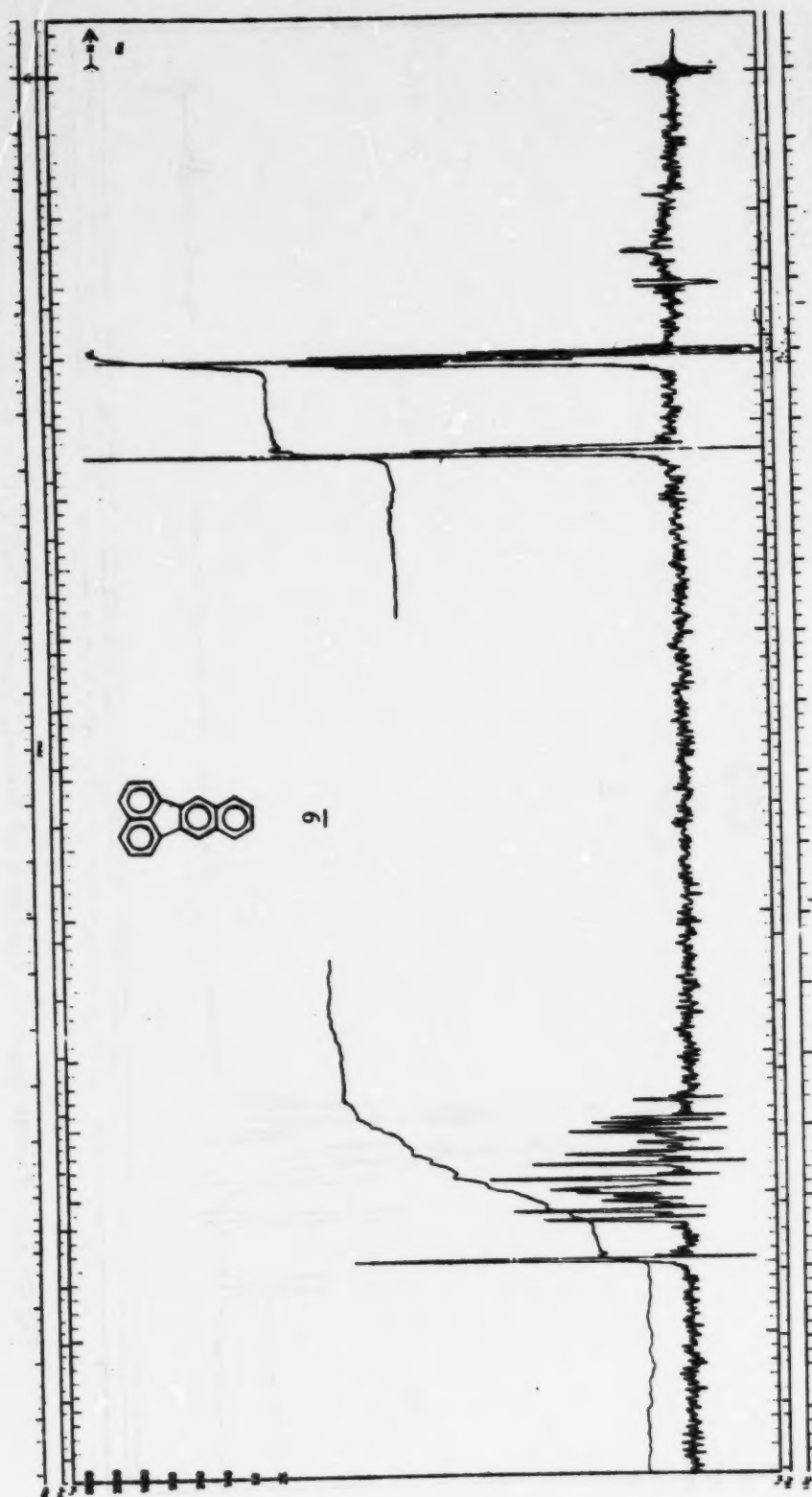


Figure 13. Proton magnetic spectrum of benzo[k]fluoranthene (9) at 100 MHz in acetonitrile. Peaks in the nonaromatic portion of the spectrum are of the solvent and solvent impurities.

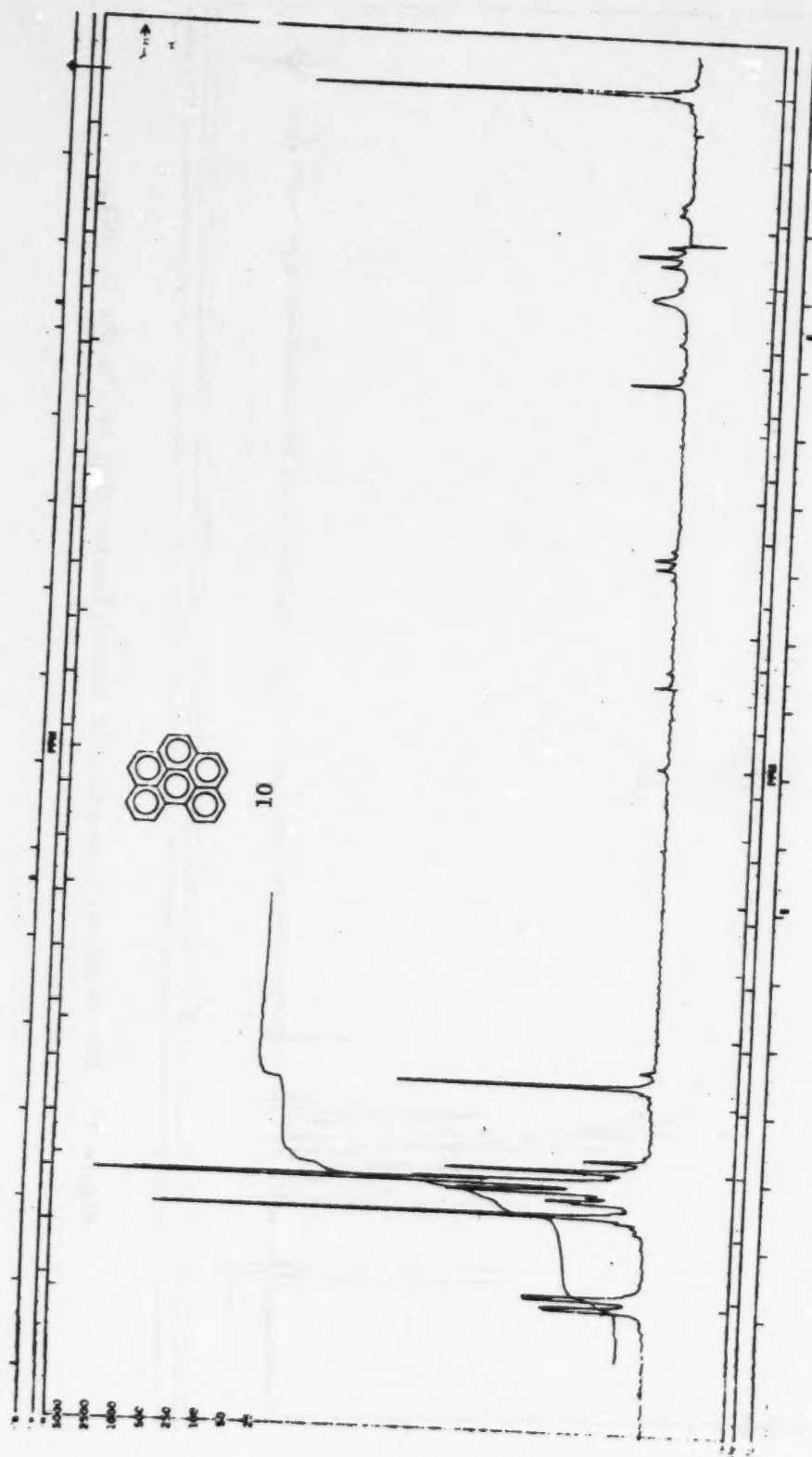


Figure 14. PMR Fourier transform spectrum of benzo[ghi]perylene (10) in CDCl₃ at 100 MHz. Peaks in the region 0-6 ppm are due to solvent impurities.

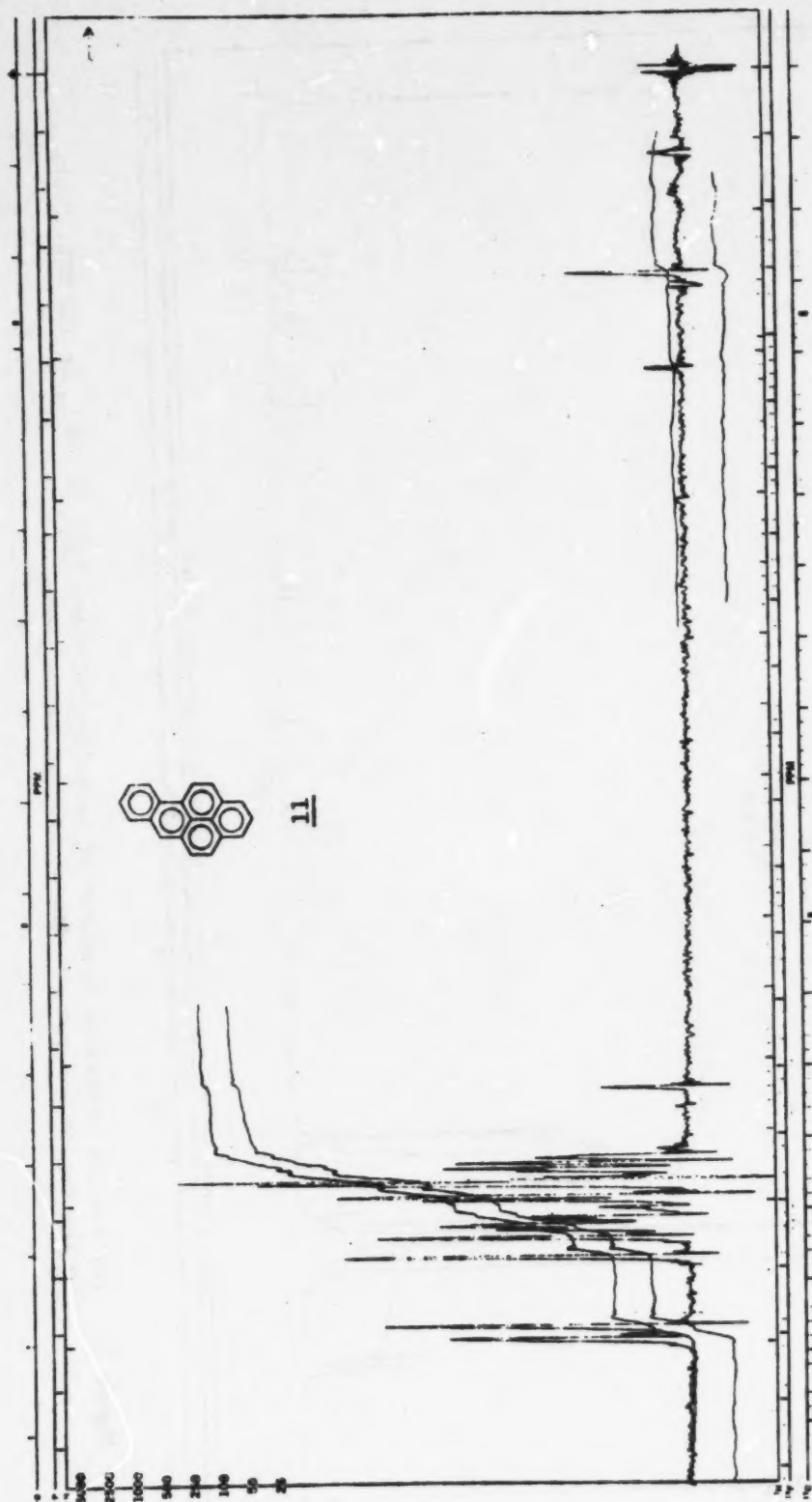


Figure 15. Proton magnetic spectrum of benzo[a]pyrene (11) at 100 MHz in CDCl₃.

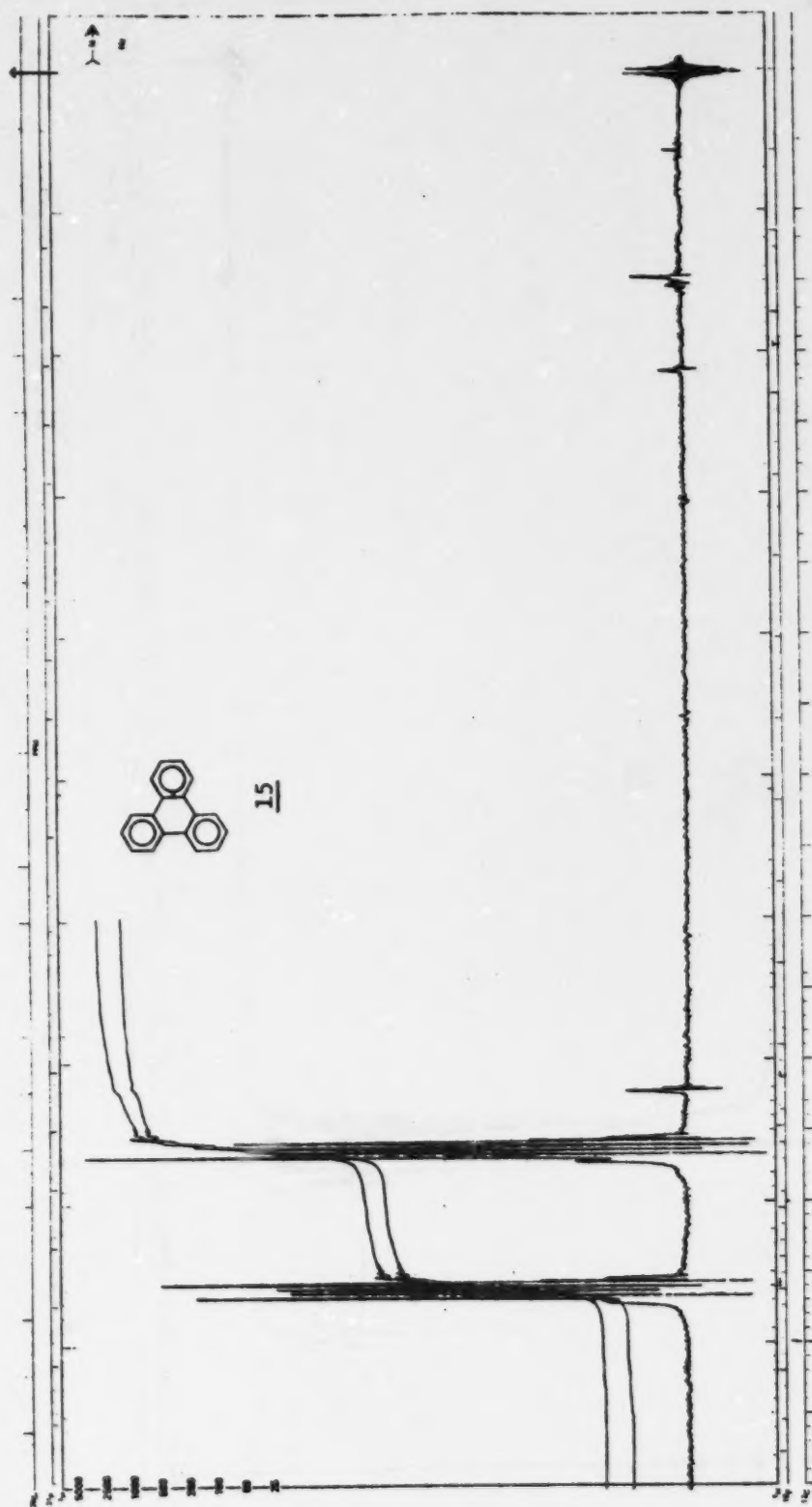


Figure 16. Proton magnetic spectrum of triphenylene (15) at 100 MHz in CDCl₃.

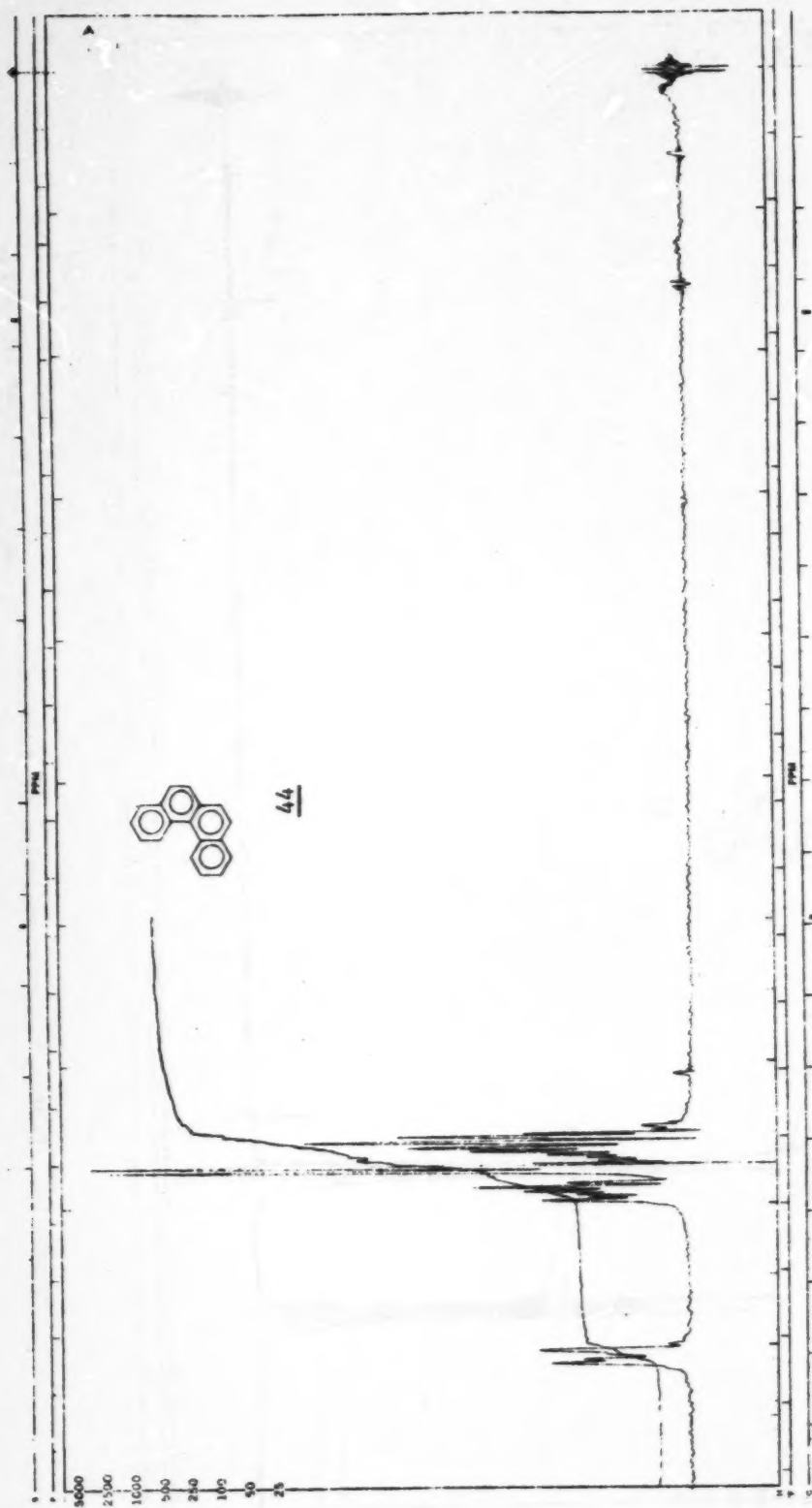


Figure 17. Proton magnetic spectrum of benzo[c]phenanthrene (44) at 100 MHz in CDCl₃.

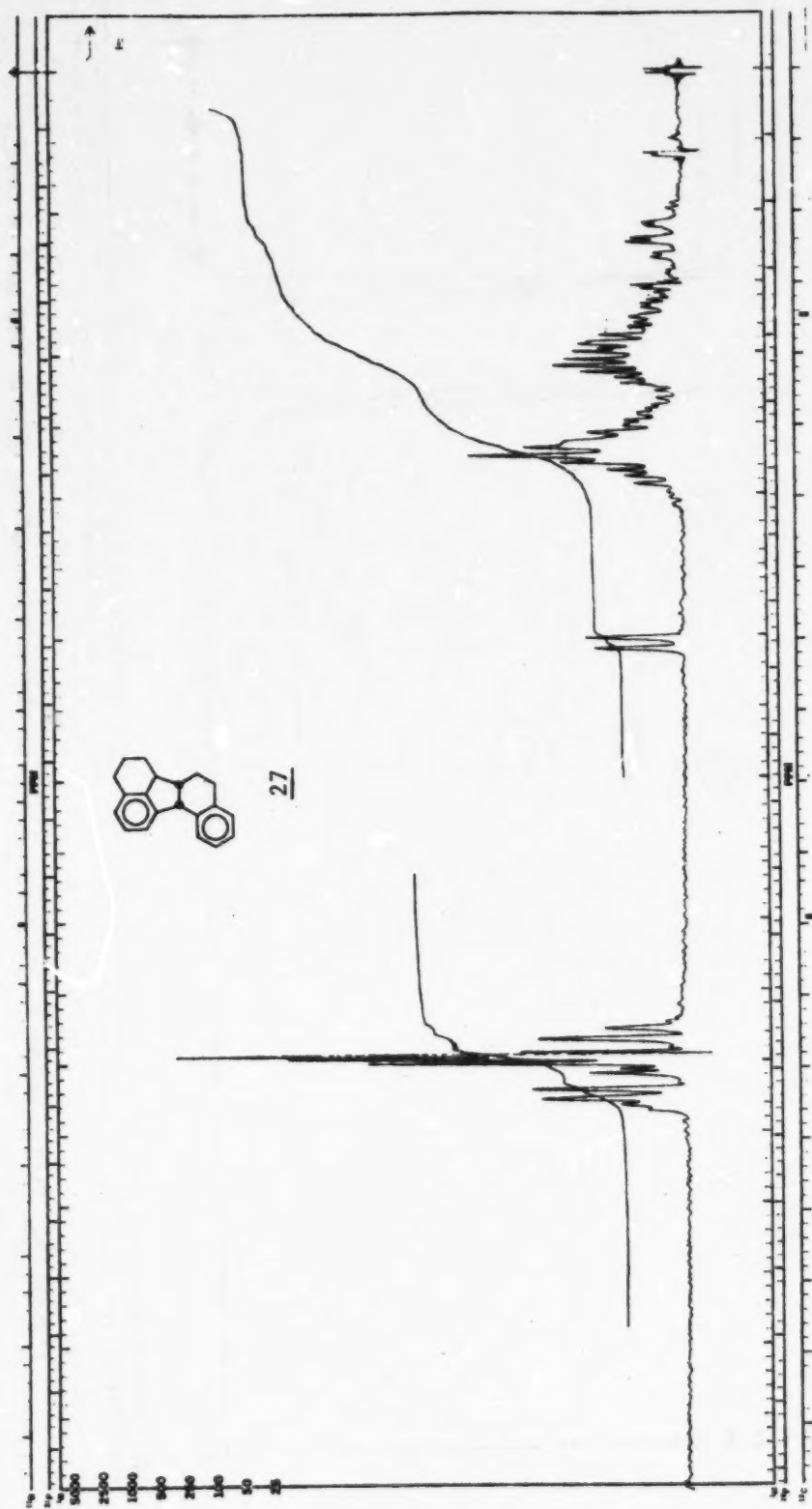


Figure 18. Proton magnetic spectrum of cis,anti-4,5,6,6a,6b,7,8,12b-octahydrobenzo[1,1']fluoranthene (27) at 100 MHz in CDCl_3 .

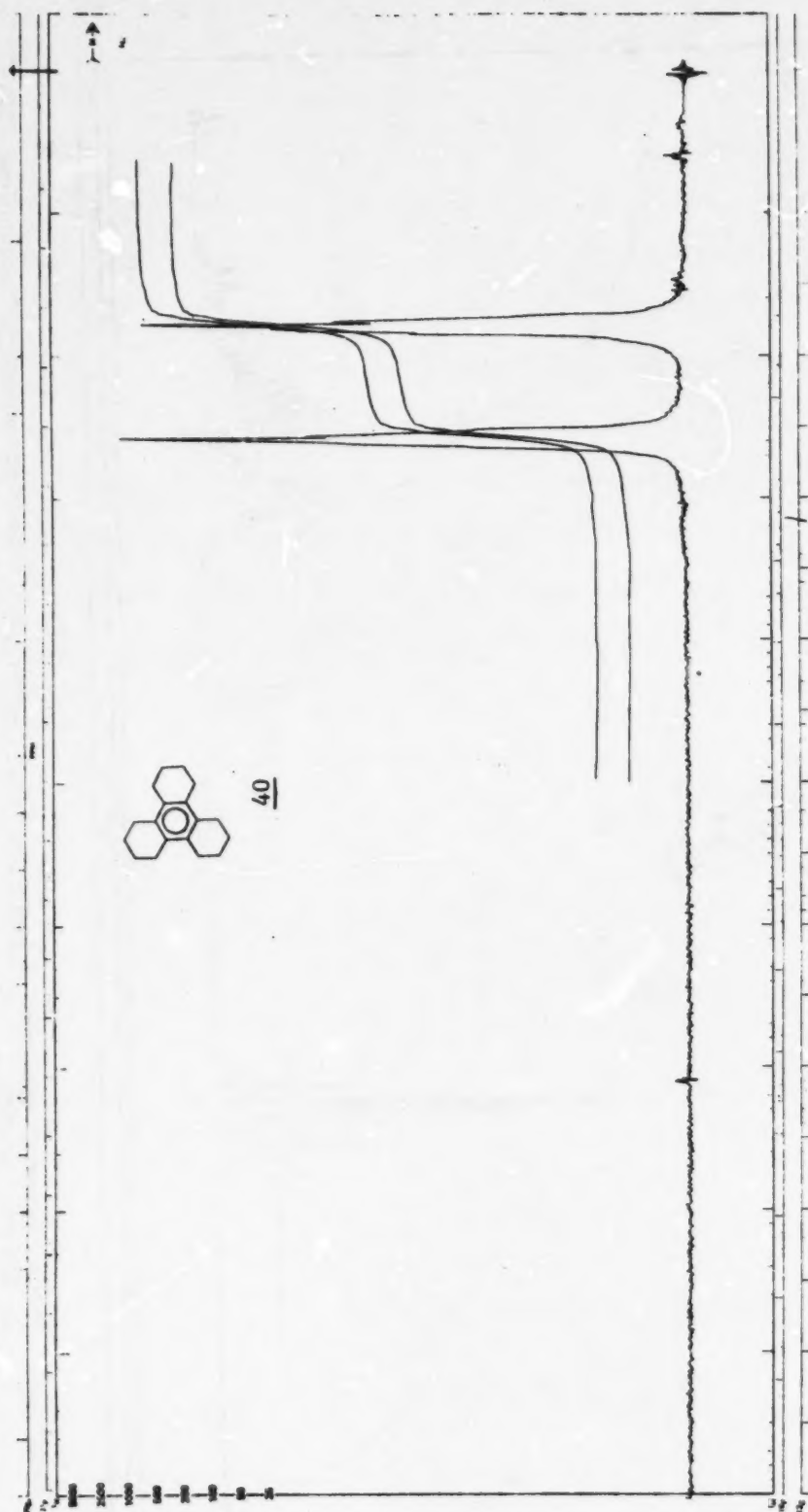


Figure 19. Proton magnetic spectrum of s-dodecahydrotriphenylene (40) at 100 MHz in CDCl_3 .

SECTION 6

RESULTS AND DISCUSSION

The objective of this project was to synthesize and purify PNA compounds, chiefly hydrocarbons, of interest to the Chemistry and Physics Laboratory, NERC, Research Triangle Park.

In Sections 4 and 5, we presented the synthesis routes and the purification techniques used in obtaining the pure samples. To avoid duplication and to foster better understanding of how the syntheses were undertaken and how the results were achieved, we commented on failures as well as successes at the time the material was presented in Section 4. However, experimental details of unsuccessful work was omitted in Section 5.

The reader specifically interested in the status of hydrocarbons supplied to the EPA is referred to pp. 1, 6, 14-22, and 23, which show the hydrocarbons obtained by purification of commercial material, those synthesized, the amounts provided and which compounds remain to be synthesized.

Our preparation of the hydrocarbons listed in Section 4 resulted in new approaches to synthesis and purification. These findings have been cited in our Quarterly Reports, described in the theses of Dr. L. L. Ansell,^{8b} Mr. F. U. Ahmed,⁹ and Mr. A. R. Taylor,¹⁴ and some of this work has been published as reported in the List of Theses and Publications (p. 60).

The salient features of this work was brought out in Sections 4 and 5. Further, as has been customary in our earlier work for the American Petroleum Institute, we have continued to provide data on the

properties of our hydrocarbons and selected intermediates to the scientific community through the Data Distribution office of the API and TRC located at Texas A&M University, College Station, Texas. The selfless efforts of Mr. M. C. Hamming and Dr. G. W. Keen, and more recently Mr. A. R. Taylor, of the Analytical Research Section of Continental Oil Company in obtaining the spectra, and the generosity of the Continental Oil Company, Research and Development, in sharing the data, made these contributions possible.

Some data has also become available from the publications of the Energy Relations Research Group of the U. S. Energy Research Center at Bartlesville Okla. This group was directed by Dr. D. R. Douslin and now by Mr. W. D. Good.

Since the samples from this work were highly purified, we decided to include pmr spectra of the completed hydrocarbons as part of this report. The pmr spectrum of anthanthrene (5), however, was not included because its insolubility precluded an acceptable pmr spectrum. These spectra are shown on pp. 41-54.

FOOTNOTES AND REFERENCES

1. E. J. Eisenbraun and L. P. Varga. The Role of ^{13}C -Organic Molecules in Pollution Studies. *Pollution Technol. Int.*, 6, 34 (1972).
2. E. J. Eisenbraun, T. E. Webb, J. W. Brunham, and L. E. Harris. An Efficient Technique for the Cleavage of Hydrocarbon Picrates. The Purification of 1,8-, 2,6-, and 2,7-Dimethylnaphthalene. *Org. Prep. Proc. Int.*, 3, 249 (1971).
3. C. E. Browne, W. L. Buchanan, and E. J. Eisenbraun. An Improved Soxhlet Apparatus. *Chem. Ind. (London)*, 35 (1977).
4. K. D. Cowan, L. L. Ansell and E. J. Eisenbraun. Separation of Anthracene Hydrogenation Products on a Picric Acid Column. *Chem. Ind. (London)*, 957 (1976).
5. K. D. Cowan and E. J. Eisenbraun. Soxhlet Extraction as a Safety Feature in the Synthesis of Polynuclear Aromatic Hydrocarbons. *Chem. Ind. (London)*, 46 (1975).
6. L. L. Ansell and E. J. Eisenbraun. An Apparatus and Procedure to Clean Sintered-Disc Buchner Funnels. *Chem. Ind. (London)*, 44 (1975).
7. R. Scholl and K. Meyer. *Ber.*, 67b, 1229 (1934).
8. a) L. L. Ansell, T. Rangarajan, W. M. Burgess, E. J. Eisenbraun, G. W. Keen and M. C. Hamming. *Org. Prep. Proc. Int.*, 8, 133 (1976).
b) L. L. Ansell, Ph.D. Thesis, Oklahoma State University, 1976, 63 pp.
9. F. U. Ahmed, M. S. Thesis, Oklahoma State University, 1975, 60 pp.
10. F. U. Ahmed, T. Rangarajan, E. J. Eisenbraun, G. W. Keen, and M. C. Hamming. *Org. Prep. Proc. Int.*, 7, 267 (1975).
11. P. H. Groggins and H. P. Newton. *Ind. Eng. Chem.*, 22, 157 (1930).
12. H. R. Snyder and F. X. Werber. *J. Am. Chem. Soc.*, 72, 2965 (1950).
13. E. Clar. *Polycyclic Hydrocarbons*, Vol. 2, Academic Press, New York, 1964.
14. A. R. Taylor, M. S. Thesis, Oklahoma State University, 1974, 73 pp.

15. D. V. Hertzler, E. J. Eisenbraun, and P.W.K. Flanagan. Chem. Ind. (London), 877 (1969).
16. Unpublished work of T. K. Dobbs, of these laboratories.
17. M. Orchin and L. Reggel. J. Am. Chem. Soc., 73, 436 (1951).
18. Unpublished work of E. H. Vickery, of these laboratories.
19. Y. Altman and D. Ginsburg, J. Chem. Soc., 466 (1959).
20. Unpublished work of C. E. Browne, of these laboratories.
21. L. M. Fieser and Mary Fieser, J. Am. Chem. Soc., 57, 782 (1935).
22. Unpublished work of T. Rangarajan, of these laboratories.
23. Unpublished work of L. L. Ansell, of these laboratories.
24. Unpublished work of A. G. Holba, of these laboratories.
25. Unpublished work of N. R. Beller, of these laboratories.
26. I. M. Aigken and D. H. Reid, J. Chem. Soc., 3487 (1956).
27. F. A. Mason, Ind. Chemist, 137 (1929).
28. a) S. V. Svetozarskii, E. W. Zil'berman, and G. A. Razuvaev, Zhur. Obshchei Khim., 29, 1454 (1959).
b) P. Rollin and R. Setton, C. R. Acad. Sci., Paris, Ser. C. 263 (18), 1080, 1966 (Fr.).
c) C. M. Buess and D. D. Lawson, Chem. Rev., 60, 313 (1960).
29. Unpublished work of P. Vuppalapaty, of these laboratories.
30. The preparation of hydrocarbons 15 and 40 was jointly sponsored by EPA and API. We thank the Thermodynamics Research Group of the U.S. ERDA Center at Bartlesville, Oklahoma, for informing us that combustion calorimetry showed the percent carbon of 15 and 40 to be $99.99 \pm 0.005\%$ and $99.99 \pm 0.003\%$ respectively.
31. J. Szmuskovisz and E. J. Modest, J. Am. Chem. Soc., 70, 2542 (1948).
32. Unpublished work of K. D. Cowan, of these laboratories.
33. a) Gas chromatographic analyses were carried out with a Hewlett-Packard Model 5750B instrument equipped with dual-flame ionization detection using 0.25-in. or 0.125-in. x 10-ft columns filled with 80-100 mesh Chromosorb G (acid-washed and DMCS-treated) coated with 5% silicone rubber UC W-98. 1.5% OV-17 + 2% QF-1 on Chrom. Q 80-100 mesh was also used as a column packing.

- b) Nuclear magnetic resonance spectra were obtained from a Varian XL-100 spectrometer.
 - c) Mass spectra were obtained from a Consolidated Electrodynamics spectrometer operated under low and high resolution conditions.
 - d) Pd/C and Rh/C catalysts were obtained from commercial sources.
 - e) Phillips Chemical Company, isohexane bp 55-60°.
34. We thank James E. Meeker for calling this to our attention.
35. D. M. Jewell and J. W. Bunger, *J. Heterocycl. Chem.*, 8, 333 (1971).
36. O. C. Dermer and J. King., *J. Am. Chem. Soc.*, 63, 3232 (1941).

LIST OF THESES AND PUBLICATIONS

Theses

A. R. Taylor, "I. Synthesis of 1,1,3-Trimethyl-3-Phenylindan and the Synthesis and Chemistry of 1-Methyl-3-Phenylindan and the Corresponding Indenes. II. Synthesis and Purification of Fulvenes and Benzo[b]fluoranthene," M.S. Thesis, Oklahoma State University, 1974, 73 pp.

F. U. Ahmed, "I. Synthesis and Purification of Benz[a]anthracene. II. Friedel-Crafts Reaction Applied to Aromatic Ethers and Crotonic Acid," M.S. Thesis, Oklahoma State University, 1975, 60 pp.

L. L. Ansell, "I. Synthesis of 4-, 5-, and 6-Ring Polynuclear Aromatic Hydrocarbons. II. Sodium-Amine Reactions of Naphthalenes: Cyclodimerization and Reductive Cyclodimerization," Ph.D. Thesis, Oklahoma State University, 1976, 63 pp.

Publications

L. L. Ansell and E. J. Eisenbraun, "An Apparatus and Procedure to Clean Sintered-Disc Buchner Funnels," Chem. Ind. (London), 44 (1975).

K. D. Cowan and E. J. Eisenbraun, "Soxhlet Extraction as a Safety Feature in the Synthesis of Polynuclear Aromatic Hydrocarbons," Chem. Ind. (London), 46 (1975).

F. U. Ahmed, T. Rangarajan, E. J. Eisenbraun, G. W. Keen, and M. C. Hamming, "The Synthesis of Benz[a]anthracene," Org. Prep. Proc. Int., 7, 267 (1975).

L. L. Ansell, T. Rangarajan, W. M. Burgess, E. J. Eisenbraun, G. W. Keen, and M. C. Hamming, "The Synthesis of 1,2,3,7,8,9-Hexahydrodibenzo[def,mno]chrysene and the Use of Hydriodic Acid-red Phosphorous in the Deoxygenation of Ketones," Org. Prep. Proc. Int., 8, 133 (1976).

K. D. Cowan, L. L. Ansell, and E. J. Eisenbraun, "Separation of Anthracene Hydrogenation Products on a Picric Acid Column," Chem. Ind. (London), 957 (1976).

C. E. Browne, W. L. Buchanan, and E. J. Eisenbraun, "An Improved Soxhlet Apparatus," Chem. Ind. (London), 35 (1977).